



Preparation and surface active properties of α -acyloxysuccinic acid derivatives from malic acid and fatty acids of crude rice bran oil

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RESUMEN

Preparación y propiedades de tensión superficial de derivados del ácido α -aciloxisuccínico a partir de derivados del ácido málico y ácidos grasos del aceite de germen de arroz.

Se han preparado compuestos de tensión superficial a partir de ácido málico por esterificación con cloruro de acilo (ii)_{a-d} de [palmítico, esteárico, oleico, linoleico y ácidos grasos mezclados de aceite de germen de arroz (RBO) (ii)_a], en presencia de piridina como catalizador, formando (iii)_{a-e}, los cuales son convertidos a sales disódicas aniónicas (iv)_{a-e}. El derivado del ácido α -acil-oxisuccínico preparado (iii)_{a-e} fue oxipropenoilado con varios moles de óxido de propileno (n=2, 4, 6 y 8) para dar (v-ix)_{a-d}. Estos compuestos fueron convertidos en tensioactivos no iónicos con dos grupos amida oxima terminal (xv-xix)_{a-d} como agregaciones moleculares y agentes tensioactivos en medio acuoso. Las estructuras se confirmaron por microanálisis, IR y espectros de ¹H NMR. Las propiedades tensioactivas de los compuestos preparados revelaron excelentes resultados.

PALABRAS-CLAVE: Aceite de germen de arroz – Acido α -aciloxisuccínico (derivados) - Acido málico (derivados) - Tensión superficial.

SUMMARY

Preparation and surface active properties of α -acyloxysuccinic acid derivatives from malic acid and fatty acids of crude rice bran oil.

Surface active compounds were prepared from malic acid by esterification with acyl chloride (ii)_{a-d}, of [palmitic, stearic, oleic, linoleic and mixed fatty acids of rice bran oil (RBO) (ii)_a], in the presence of pyridine as catalyst, forming (iii)_{a-e}, which are converted to anionic disodium salt (iv)_{a-e}. The prepared α -acyl-oxysuccinic acid derivatives (iii)_{a-e}, was oxypropenoxyated with various moles of propylene oxide (n= 2, 4, 6 and 8) to give (v-ix)_{a-d}. These compounds were converted to nonionic surfactants with two terminal amide oxime groups (xv-xix)_{a-d} as molecular aggregations and surface active agents in aqueous media. The structures were confirmed by micro analysis, IR and ¹H NMR spectra. The surface active properties of the prepared compounds revealed excellent results.

KEY-WORDS: α -acyloxysuccinic acid (derivatives) - Crude rice bran oil - Malic acid (derivatives) - Surface activity.

1. INTRODUCTION

Locally produced nonedible oil, namely rice bran oil (RBO) was utilized as starting material for

preparing some anionic [1] and nonionic surface active agents with an amide oxime function group [2], which have gained major interest for preparation of complex with uranium; gallium and various transition metal ions [3-4]. There are some reports on the recovery of uranium from sea water by amide oxime polymers or the separation of various transition metals by telomer type surface active amide oxime such as ion flotation collectors [5], or the concentration of gallium from the Bayer's solution by amide oxime [6]. It was reported that, terminal amide oxime group seemed to contribute to be hydrophilic property [7]. So attention was focused on the preparation of a novel types of surfactants with an amide oxime terminal group from dicarboxylic acid esters prepared from fatty acids of nonedible rice bran oil to make a double function surfactant and as molecular aggregations. Amide oxime was prepared from nitriles obtained by cyano-ethylation of the adduct of dicarboxylic acid with various moles of propylene oxide (2,4,6 and 8 mole). The synthetic root of amide oxime and abbreviations of compounds are shown (cf. Scheme 1).

2. MATERIAL AND METHODS

All melting points are uncorrected. The IR spectrum was measured by a Pye Unicam SR-1000 infrared spectrophotometer as Nujol mull and proton nuclear magnetic resonance (¹H NMR) was done in CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard [Varian EM-390] spectrophotometer operating at 90 MHz. Microanalysis was conducted to confirm the structure of the prepared compounds.

2.1. Fatty acid composition of rice bran oil

Was determined according to El-Sawy [8].

2.2. Fatty acid chlorides (ii)_{a-e}

Were prepared as viscous oil from the corresponding acids (palmitic, stearic, oleic, linoleic

and mixed acids of rice bran oil) according to Youngs *et al.* method [9].

2.3. Fatty α -acyloxysuccinic acid derivatives (iii)_{a-e}

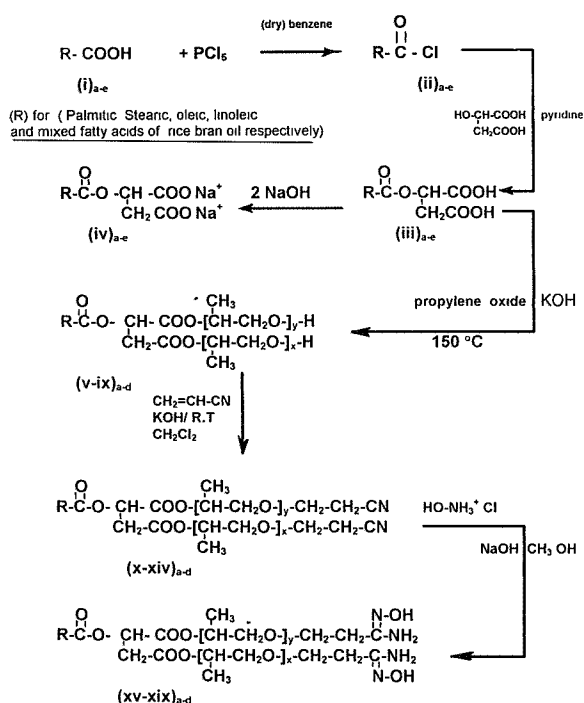
Were prepared by esterification of the fatty acid chloride with malic acid according to Nakamura *et al.* [10]. The prepared acids were neutralized using sodium hydroxide (2 N) to afforded (iv)_{a-e} as anionic surface active agents.

2.4. Oxypropenoxylation of fatty α -acyloxy succinic acid derivatives (v-ix)_{a-d}

The procedure was described by El-Sawy *et al.* [11]. The fatty α -acyloxysuccinic acid derivatives (iii)_{a-e}, propylene oxide and KOH were charged to propenoxylation apparatus. The structure of the prepared compounds was confirmed by micro analysis and spectral data.

2.5. Fatty oxypropionitrile (x-xiv)_{a-d}

The typical procedure was illustrated by Masuyama *et al.* [7]. The structure of the prepared compounds was confirmed by micro analysis .



Where:

(v-ix)_a, (x-xiv)_a and (xv-xix)_a
 (v-ix)_b, (x-xiv)_b and (xv-xix)_b
 (v-ix)_c, (x-xiv)_c and (xv-xix)_c
 (v-ix)_d, (x-xiv)_d and (xv-xix)_d

x+y = 2
 x+y = 4
 x+y = 6
 x+y = 8

Scheme 1

2.6. Fatty oxypropione amide oxime (xv-xix)_{a-d}

Hydroxylamine hydrochloride (7 gm.100 m.mol.) in MeOH 30 ml was add to NaOH (4.0 gm. 100 m.mol.) in 30 ml. MeOH at room temperature, and insoluble solids were separated off by filtration. To this filtrate (40 m.mol.) of the prepared fatty nitrile in 40 ml. of methanol was dropped and the mixture was stirred at room temperature for about 24 hours (pH =5-7) under these conditions [7]. After filtration and subsequent evaporation of filtrate, 50 ml of (CH₂Cl₂) was added to the residue. Insoluble solids were filtered off again, and the crude product was obtained by evaporation of solvent. The product was confirmed by micro analysis and spectral data.

2.7. Surface properties

2.7.1. Surface and interfacial tensions

Were measured using Du-Nouy tensiometer [12] (Kruss, Type 8451), with 0.1 wt % aqueous solution at room temperature (25°C).

2.7.2. Kraft point

Of the prepared anionic surfactants was measured as the temperature where 1% dispersion becomes clear on gradual heating [13].

2.7.3. Cloud point

Was determined by gradually heating 1.0 wt % solution in controlled temperature bath and recording the temperature at which the clear, or nearly clear, solutions become definitely turbid. The reproducibility of this temperature was checked by cooling the solutions until they become clear again [14].

2.7.4. Wetting time

Was determined by immersing a sample of cotton fabric in 0.1 wt % aqueous solution of the surfactants [15].

2.7.5. Foaming properties

Were measured by Ross Miles [16] method. The foam production for 1.0 wt % solution was measured by the foam height initially produced.

2.7.6. Emulsion stability

The emulsion was prepared from 10 ml. of a 20 m. mol. aqueous solution of surfactant and 5 ml. of

toluene at 40°C. The emulsifying property was determined by the time its took for an aqueous volume separating from the emulsion layer to reach 9 ml. counting from the moment of the cession shaking [17].

2.7.7. Ca^{++} stability

Was determined by a modified Hurt method [18].

2.7.8. Stability to hydrolysis

A mixture of 10 m.mol. surfactant and 10 ml. 0.05N NaOH were placed in a thermostate at 40°C. The time takes by a sample solution to be clouded as

a result of hydrolysis shows the stability of surfactant to hydrolysis [1].

3. RESULTS AND DISCUSSION

Preparation of fatty α -acyloxysuccinic acid derivatives (iii)_{a-e}, oxypropenoxylated fatty α -acyloxysuccinic acid derivatives (v-ix)_{a-d}, fatty oxypropionitrile (x-xiv)_{a-d} and fatty amide oxime (xv-xix)_{a-d} was easy and could be isolated in suitable yield (cf. Tables I-III); infra red (IR) and proton nuclear magnetic resonance (¹H NMR) spectroscopic analysis were conducted to confirm the structure of some examples of the prepared compounds (cf. Table IV).

Table I
Micro analysis of the prepared α -acyloxy succinic acids (iii)_{a-e} and propenoxylated α -acyloxysuccinate (v-ix)_{a-d}

Compd. no.	n=x+y PO	Mol. Formula	M.P. °C	Mol.Wt	Micro analysis				
					C%		H%		
					Calc.	Fd.	Calc.	Fd.	
iii _a	C _{16.0}	C ₂₀ H ₃₆ O ₆	43-45	372	64.51	64.20	9.67	8.60	
iii _b	C _{18.0}	C ₂₂ H ₄₀ O ₆	47-49	400	66.00	65.60	10.00	9.10	
iii _c	C _{18.1}	C ₂₂ H ₃₈ O ₆	37-39	398	66.33	66.00	9.54	8.70	
iii _d	C _{18.2}	C ₂₂ H ₃₆ O ₆	33-35	396	66.66	66.00	9.09	7.80	
iii _e	mixed	**	visc. oil	**	**	65.10	**	9.80	
C _{16:0} :	va	2	C ₂₆ H ₄₈ O ₈	30-32	488	63.93	63.40	9.83	9.00
	b	4	C ₃₂ H ₆₀ O ₁₀	visc. oil	604	63.57	63.00	9.93	9.40
	c	6	C ₃₈ H ₇₂ O ₁₂	visc. oil	720	63.33	62.30	10.00	9.90
	d	8	C ₄₄ H ₈₄ O ₁₄	visc. oil	836	63.15	62.80	10.04	10.00
C _{18:0} :	via	2	C ₂₈ H ₅₂ O ₈	34-36	516	65.11	64.20	10.07	9.70
	b	4	C ₃₄ H ₆₄ O ₁₀	visc. oil	632	64.55	64.10	10.12	10.10
	c	6	C ₄₀ H ₇₆ O ₁₂	visc. oil	748	64.17	63.80	10.16	9.70
	d	8	C ₄₆ H ₈₈ O ₁₄	visc. oil	864	63.88	64.00	10.18	10.10
C _{18:1} :	vii _a	2	C ₂₈ H ₅₀ O ₈	visc. oil	514	65.36	65.10	9.72	9.60
	b	4	C ₃₄ H ₆₂ O ₁₀	visc. oil	630	64.76	64.00	9.84	9.50
	c	6	C ₄₀ H ₇₄ O ₁₂	visc. oil	746	64.34	63.70	9.91	9.40
	d	8	C ₄₆ H ₈₆ O ₁₄	visc. oil	862	64.03	63.40	9.97	9.80
C _{18:2} :	viii _a	2	C ₂₈ H ₄₈ O ₈	visc. oil	512	65.62	65.00	9.37	9.00
	b	4	C ₃₄ H ₆₀ O ₁₀	visc. oil	628	64.96	64.00	9.55	9.20
	c	6	C ₄₀ H ₇₂ O ₁₂	visc. oil	744	64.51	63.50	9.67	9.60
	d	8	C ₄₆ H ₈₄ O ₁₄	visc. oil	860	64.18	63.10	9.76	8.80
mixed:	ix _a	2	**	visc. oil	**	**	64.00	**	9.30
	b	4	**	visc. oil	**	**	64.30	**	10.20
	c	6	**	visc. oil	**	**	65.00	**	9.80
	d	8	**	visc. oil	**	**	63.90	**	8.90

** Mixed α -acyloxysuccinate of rice bran oil.

Table II
Micro analysis of the prepared oxypropionitriles of α -acyloxysuccinate(x-xiv)_{a-d}

Compd. no.	n=x+y PO	Mol. Formula	Mol.Wt	Micro analysis							
				C%		H%		N%			
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.		
C _{16:0}	x	a	2	C ₃₂ H ₅₄ N ₂ O ₈	594	64.64	63.80	9.09	9.00	4.70	4.20
		b	4	C ₃₈ H ₆₈ N ₂ O ₁₀	710	64.22	63.60	9.29	9.10	3.94	3.20
		c	6	C ₄₄ H ₇₈ N ₂ O ₁₂	826	63.92	62.90	9.44	9.30	3.38	3.30
		d	8	C ₅₀ H ₉₀ N ₂ O ₁₄	942	63.69	63.00	9.55	9.50	2.97	2.50
C _{18:0}	xi	a	2	C ₃₄ H ₅₈ N ₂ O ₈	622	65.59	64.90	9.32	9.20	4.50	4.10
		b	4	C ₄₀ H ₇₀ N ₂ O ₁₀	738	65.04	65.00	9.48	9.30	3.79	3.10
		c	6	C ₄₆ H ₈₂ N ₂ O ₁₂	854	64.63	64.50	9.60	9.50	3.27	3.10
		d	8	C ₅₂ H ₉₄ N ₂ O ₁₄	970	64.32	64.00	9.69	9.60	2.88	2.50
C _{18:1}	xii	a	2	C ₃₄ H ₅₆ N ₂ O ₈	620	65.80	65.10	9.03	8.00	4.51	4.00
		b	4	C ₄₀ H ₆₈ N ₂ O ₁₀	736	65.21	65.00	9.23	9.00	3.80	3.10
		c	6	C ₄₆ H ₈₀ N ₂ O ₁₂	852	64.78	63.90	9.38	8.60	3.28	3.00
		d	8	C ₅₂ H ₉₂ N ₂ O ₁₄	968	64.46	64.20	9.50	9.40	2.89	2.40
C _{18:2}	xiii	a	2	C ₃₄ H ₅₄ N ₂ O ₈	618	66.01	66.00	8.73	8.00	4.53	4.10
		b	4	C ₄₀ H ₆₆ N ₂ O ₁₀	734	65.39	65.00	8.99	8.40	3.81	3.30
		c	6	C ₄₆ H ₇₈ N ₂ O ₁₂	850	64.94	64.30	9.17	9.00	3.29	3.00
		d	8	C ₅₂ H ₉₀ N ₂ O ₁₄	966	64.59	64.40	9.31	8.80	2.89	2.60
mixed: xiv	a	a	2	**	**	**	64.50	**	9.10	**	3.30
		b	4	**	**	**	63.90	**	8.60	**	3.10
		c	6	**	**	**	64.30	**	9.30	**	2.80
		d	8	**	**	**	63.00	**	8.90	**	2.70

** Mixed nitrile of α -acyloxysuccinate of rice bran oil.

Table III
Micro analysis of the amide oxime for oxypropenoxylated α -acyloxysuccinate (xv-xix)_{a-d}

Compd. no.	n=x+y PO	Mol. Formula	Mol.Wt	Micro analysis							
				C%		H%		N%			
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.		
C _{16:0}	xv	a	2	C ₃₂ H ₆₀ N ₄ O ₁₀	660	58.18	57.90	9.09	8.90	8.48	8.50
		b	4	C ₃₈ H ₇₂ N ₄ O ₁₂	776	58.76	57.80	9.27	9.00	7.21	6.90
		c	6	C ₄₄ H ₈₄ N ₄ O ₁₄	892	59.19	59.00	9.41	9.30	6.27	6.00
		d	8	C ₅₀ H ₉₆ N ₄ O ₁₆	1008	59.52	59.30	9.52	9.30	5.55	5.00
C _{18:0}	xvi	a	2	C ₃₄ H ₆₄ N ₄ O ₁₀	688	59.30	57.00	9.30	9.00	8.13	7.90
		b	4	C ₄₀ H ₇₆ N ₄ O ₁₂	804	59.70	59.20	9.45	9.70	6.96	6.10
		c	6	C ₄₆ H ₈₈ N ₄ O ₁₄	920	59.78	59.60	9.56	8.50	6.08	5.60
		d	8	C ₅₂ H ₁₀₀ N ₄ O ₁₆	1036	60.23	60.00	9.65	9.20	5.40	5.00
C _{18:1}	xvii	a	2	C ₃₄ H ₆₂ N ₄ O ₁₀	686	59.47	59.40	9.03	8.90	8.16	8.00
		b	4	C ₄₀ H ₇₄ N ₄ O ₁₂	802	59.85	59.20	9.22	9.00	6.98	6.30
		c	6	C ₄₆ H ₈₆ N ₄ O ₁₄	918	60.13	59.00	9.36	9.10	6.10	6.00
		d	8	C ₅₂ H ₉₈ N ₄ O ₁₆	1034	60.34	59.00	9.47	9.20	5.41	5.00
C _{18:2}	xviii	a	2	C ₃₄ H ₆₀ N ₄ O ₁₀	684	59.64	59.00	8.77	7.70	8.18	8.00
		b	4	C ₄₀ H ₇₂ N ₄ O ₁₂	800	60.00	59.10	9.00	8.50	7.00	6.60
		c	6	C ₄₆ H ₈₄ N ₄ O ₁₄	916	60.26	60.00	9.17	9.00	6.11	5.70
		d	8	C ₅₂ H ₉₆ N ₄ O ₁₆	1032	60.46	60.00	9.30	9.00	5.42	4.40
mixed: xix	a	a	2	**	**	**	60.00	**	6.90	**	7.50
		b	4	**	**	**	61.10	**	7.50	**	6.70
		c	6	**	**	**	61.20	**	8.70	**	5.40
		d	8	**	**	**	61.20	**	8.90	**	4.20

** Mixed amide oxime of α -acyloxysuccinate of rice bran oil.

Table IV
Spectral data for some examples of the prepared α -acyloxysuccinic acids derivatives

Compound no.	Mol. formula	^1H MNR (ppm)	IR (cm^{-1})
C _{16:0} (iii)a	C ₂₀ H ₃₆ O ₆	$\delta=0.9$ (t.3H,terminal CH ₃), $\delta=1.1-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, CH ₂ -CH ₂ CO), $\delta=2.0$ (d., CH ₂ -CH-COOH), $\delta=4.1$ (t., 1H, R.COOCH-CO-), and disappearing of carboxylic proton may be due to the intramolecular hydrogen bond	broad peak at 3500-2550 cm^{-1} ν OH of acid, 1740 cm^{-1} ester 1700 cm^{-1} ν CO of acid
C _{18:1} (iii)c	C ₂₂ H ₃₈ O ₆	$\delta=0.8$ (t.3H,terminal CH ₃), $\delta=1.0-1.3$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, CH ₂ -CH ₂ CO), $\delta=2.0$ (d., CH ₂ -CH-COOH), $\delta=4.1$ (t.1H, R.COOCH-COOH), $\delta=5.4$ (br. singlet 2H, olefinic proton), and disappearing of carboxylic proton may be due to the intramolecular hydrogen bond	broad peak at 3500-2550 cm^{-1} ν OH of acid, 2970 cm^{-1} , 2920, 2860 cm^{-1} ν CH aliphatic, 1740 cm^{-1} ν CO of ester 1700 cm^{-1} ν CO of acid and 1630 cm^{-1} ν C=C
C _{18:2} (iii)d	C ₂₂ H ₃₆ O ₆	$\delta=0.9$ (t.3H,terminal CH ₃), $\delta=1.0-1.3$ (br. singlet, (CH ₂) chain), $\delta=1.7$ (t, CH ₂ -CH ₂ CO), $\delta=2.1$ (d., CH ₂ -CH-COOH), $\delta=2.8$ (t., 2H, -CH=CH-CH ₂ -CH=CH-), $\delta=4.3$ (t., 1H, R.COOCH-COOH), $\delta=5.4$ (br. singlet 4H, olefinic proton), and disappearing of carboxylic proton may be due to the intramolecular hydrogen bond	broad peak at 3500-2500 cm^{-1} ν OH of acid, 1735 cm^{-1} ν CO of ester 1700 cm^{-1} ν CO of acid and 1640 cm^{-1} ν C=C
C _{16:0} (v)c	C ₃₈ H ₇₂ O ₁₂	$\delta=0.8$ (t.3H,terminal CH ₃), $\delta=1.1$ (d. 18H,COOCH (CH ₃) CH ₂), $\delta=1.2-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, CH ₂ -CH ₂ CO), $\delta=2.3$ (d., OCCH ₂ -CH-CO), $\delta=3.2-3.8$ (m. 18H, 2CO(OCH(CH ₃)(CH ₂) ₃), $\delta=4.1$ (t. 1H, R.COOCH-CO-), and $\delta=4.8$ (br. singlete 2H, COOCH(CH ₃)CH-OH).	3460 cm^{-1} ν OH of hydroxy ester, 2960 cm^{-1} characteristic for ν CH aliphatic, 1735 cm^{-1} ν C=O of ester, and 1450, 1260, 1090 cm^{-1} characteristics for ν C-O-C.
C _{18:0} (vi)a	C ₂₈ H ₅₂ O ₈	$\delta=0.85$ (t.3H,terminal CH ₃), $\delta=1.1$ (d. 6H,COOCH (CH ₃) (CH ₂), $\delta=1.2-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, CH ₂ -CH ₂ CO), $\delta=2.3$ (d., OCCH ₂ -CH-CO), $\delta=3.2-3.8$ (m. 6H, 2CO(OCH(CH ₃)(CH ₂), $\delta=4.0$ (t. 1H, R.COOCH-CO-), and $\delta=4.9$ (br. singlete 2H, COOCH(CH ₃)CH-OH).	3460 cm^{-1} ν OH of hydroxy ester, 2970 cm^{-1} characteristic for ν CH aliphatic, 1740 cm^{-1} ν C=O of ester, and 1450, 1250, 1090 cm^{-1} characteristics for ν C-O-C.
C _{18:0} (vi)b	C ₃₄ H ₆₄ O ₁₀	$\delta=0.8$ (t.3H,terminal CH ₃), $\delta=1.1$ (d. 12H,COOCH (CH ₃) (CH ₂), $\delta=1.2-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, CH ₂ -CH ₂ CO), $\delta=2.3$ (d., 2H, OCCH ₂ -CH-CO), $\delta=3.2-3.8$ (m. 12H, 2CO(OCH(CH ₃)(CH ₂) ₂), $\delta=4.2$ (t. 1H, R.COOCH-CO-), and $\delta=4.7$ (br. singlete 2H, COOCH(CH ₃)CH-OH).	3470 cm^{-1} ν OH of hydroxy ester, 2960 cm^{-1} characteristic for ν CH aliphatic, 1735 cm^{-1} ν C=O of ester, and 1450, 1240, 1100 cm^{-1} characteristics for ν C-O-C.
C _{18:2} (viii)d	C ₄₆ H ₈₄ O ₁₄	$\delta=0.8$ (t.3H,terminal CH ₃), $\delta=1.2$ (d. 24H,COOCH (CH ₃) (CH ₂)), $\delta=1.2-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, 2H CH ₂ -CH ₂ CO), $\delta=2.3$ (d., OCCH ₂ -CH-CO), $\delta=2.7$ (t., 2H, -CH=CH-CH ₂ -CH=CH-), $\delta=3.2-3.8$ (m. 24H, 2CO(OCH(CH ₃)(CH ₂) ₄), $\delta=4.0$ (t. 1H, R.COOCH-CO-), $\delta=4.9$ (br. s., 2H, COOCH(CH ₃)CH-OH), $\delta=5.4$ (br. s. olefinic proton).	3440 cm^{-1} ν OH of hydroxy ester, 3180 ν C-H olefinic, 2960 cm^{-1} characteristic for ν CH aliphatic, 1740 cm^{-1} ν C=O of ester, 1650 cm^{-1} ν C=C and 1460, 1250, 1100 cm^{-1} characteristics for ν C-O-C.
C _{mixed} (ix)d	**	$\delta=0.7$ (t.3H,terminal CH ₃), $\delta=1.1$ (d. COOCH (CH ₃)CH ₂), $\delta=1.2-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, 2H CH ₂ -CH ₂ CO), $\delta=2.3$ (d., 2H, OCCH ₂ -CH-CO), $\delta=2.6$ (t., 2H, -CH=CH-CH ₂ -CH=CH-), $\delta=3.2-3.8$ (m. 2CO, (OCH (CH ₃)(CH ₂) ₄), $\delta=4.0$ (t. 1H, R.COOCH-CO-), $\delta=4.8$ (br. s., 2H, COOCH(CH ₃)CH-OH), $\delta=5.5$ (br. singlet olefinic proton).	3460 cm^{-1} ν OH of hydroxy ester, 3180 cm^{-1} ν C-H olefinic, 2970 cm^{-1} characteristic for ν CH aliphatic, 1735 cm^{-1} ν C=O of ester, 1640 cm^{-1} ν C=C and 1460, 1250, 1100 cm^{-1} characteristics for ν C-O-C.
C _{16:0} (xv)b	C ₃₈ H ₇₂ N ₄	$\delta=0.85$ (t.3H,terminal CH ₃), $\delta=1.1-1.2$ (d. 12H,COOCH (CH ₃)-CH ₂ -O), $\delta=1.2-1.4$ (br. singlet, (CH ₂) chain), $\delta=1.6$ (t, 2H CH ₂ -CH ₂ CO), $\delta=2.3$ (d., 2H, OCCH ₂ -CH-CO), $\delta=2.6$ (t., 4H, H, 2-CH ₂ -C(NH ₂)=NOH-), $\delta=3.2-3.8$ (m. 12H, 2CO(OCH(CH ₃)(CH ₂) ₂), $\delta=4.15$ (t. 1H, R.COOCH-CO-), $\delta=4.5-4.9$ (br. s., 6H, 2CH ₂ -C(NH ₂)=NOH).	3420 cm^{-1} ν OH of oxime, 3340, 3150 cm^{-1} ν NH ₂ , 2960 cm^{-1} characteristic for ν CH aliphatic, 1740 cm^{-1} ν C=O of ester, 1670 cm^{-1} ν C=N and 1460, 1220, 1100 cm^{-1} characteristics for ν C-O-C.

Table IV (Contin.)

Compound no.	Mol. formula	¹ H MNR (ppm)	IR (cm ⁻¹)
C _{mixed} (xix) _c	**	δ=0.7 (t.3H, terminal CH ₃), δ=1.1 (d. 12HCOOCH(CH ₃)-CH ₂ -O), δ=1.2-1.4 (br. singlet, (CH ₂) chain), δ=1.6 (t, 2H CH ₂ -CH ₂ CO), δ=2.3 (d., 2H OCCH ₂ -CH-CO), δ=2.6 (t., 4H, H, 2CH ₂ -C(NH ₂)=NOH), δ=2.9 (m. 2H, -CH=CH-CH ₂ -CH=CH-), δ=3.3-3.9 (m. H, 2CO, (OCH(CH ₃)CH ₂) ₂), δ=4.1 (t. 1H, R.COOCH-(CH ₂)-CO-), δ=4.5-4.9 (br. s., 6H, 2CH ₂ -C(NH ₂)=N-OH), δ=5.5 (br. singlet olefinic proton).	3480 cm ⁻¹ νOH of oxime, 3300, 3120 cm ⁻¹ νNH ₂ , 3100 cm ⁻¹ νC-H olefinic, 2960 cm ⁻¹ characteristic for νCH aliphatic, 1740 cm ⁻¹ νC=O of ester, 1670 cm ⁻¹ νC=N, 1620 cm ⁻¹ νC=C and 1450, 1240, 1090 cm ⁻¹ characteristics for ν C-O-C.

3.1. Surface active properties

Surface active properties of the α-acyloxydisodiumsuccinate (iv)_{a-e}, propenoxylated α-acyloxy succinate ester (v-ix)_{a-d} and amide oxime (xiv-xix)_{a-e}, were determined. It was found that, the

amide oxime acted as cationic surfactants under acidic conditions and as nonionic ones under neutral and basic condition [7]. The Surface active properties of the prepared compounds were measured under neutral conditions as listed in Tables (V-VII) respectively.

Table V
Surface properties of the anionic α-acyloxy succinate derivatives (iv)_{a-e}

Compd. no.		S.T. (dyn/cm) 0.1%	I.F.T. (dyn/cm) 0.1%	Kraft point 1%	Emul. stability (Sec.)	Wetting t. (sec.) 0.1%	Foam h. (1%) (mm)	Ca ⁺⁺ Stability (ppm)	Stab. to hyd. (Base) (min:sec)
C ₁₆	iva	30.0	4.5	5.0	474.0	130.0	320.0	1300	342:15
C ₁₈	ivb	32.5	6.5	8.0	498.0	145.0	280.0	1200	368:29
C ¹ ₁₈	ivc	34.0	4.5	6.0	455.0	139.0	260.0	1400	340:19
C ² ₁₈	ivd	37.0	6.0	7.0	466.0	142.0	270.0	1400	338:43
Mixed	ive	39.5	7.5	<0	538.0	98.0	295.0	1600	348:09

Table VI
Surface properties of propenoxylated α-acyloxy succinate derivatives (v-ix)_{a-d}

Compd. no.	n	S.T. (dyn/cm) 0.1%	I.F.T. (dyn/cm) 0.1%	Cloud point 1%	Emul. stability (min:sec.)	Wetting time (sec.) 0.1%	Foam h. (1%) (mm)
C _{16:0}	v a	2	46.0	10.5	—	54:16	40.0
	b	4	42.5	7.5	52.0	51:41	80.0
	c	6	39.5	7.0	59.0	49:36	110.0
	d	8	36.5	6.0	66.0	42:08	120.0
C _{18:0}	vi a	2	47.5	12.5	—	62:23	20.0
	b	4	43.5	11.5	58.0	58:46	60.0
	c	6	40.0	10.5	62.0	51:51	95.0
	d	8	39.0	9.5	68.0	47:48	105.0
C _{18:1}	vii a	2	48.5	13.0	—	67:29	10.0
	b	4	45.5	10.5	60.0	55:33	40.0
	c	6	42.0	9.5	67.0	49:19	70.0
	d	8	40.0	8.5	73.0	47:52	90.0

Table VI (Contin.)

Compd. no.	n	S.T. (dyn/cm) 0.1%	I.F.T. (dyn/cm) 0.1%	Cloud point 1%	Emul. stability (min:sec.)	Wetting time (sec.) 0.1%	Foam h. (1%) (mm)	
C _{18:2} viii	a	2	50.0	12.0	—	70:10	260	40.0
	b	4	48.5	9.0	62.0	64:32	243	50.0
	c	6	44.5	8.0	69.0	59:29	220	80.0
	d	8	43.0	7.5	76.0	51:00	198	95.0
Mixed ix	a	2	52.0	12.0	—	87:19	239	—
	b	4	49.0	9.0	64.0	73:41	217	60.0
	c	6	45.0	8.5	69.0	69:38	197	85.0
	d	8	42.0	7.0	71.0	59:22	180	100.0

Table VII

Surface properties of the amide oxime propenoxyated α -acyloxysuccinate derivatives (xv-xix)_{a-d}

Compd. no.	n	S.T. (dyn/cm) 0.1%	I.F.T. (dyn/cm) 0.1%	Cloud point 1%	Emul. stability (min:sec.)	Wetting time (sec.) 0.1%	Foam h. (1%) (mm)	
C _{16:0} xv	a	2	39.0	9.5	52.0	70:30	120	10.0
	b	4	37.5	7.5	95.0	66:41	102	40.0
	c	6	34.0	5.5	>100	60:43	74.0	65.0
	d	8	32.0	4.5	>100	54:19	56.0	85.0
C _{18:0} xvi	a	2	42.5	12.0	63.0	87:23	142	—
	b	4	39.5	11.5	95.0	79:46	123	30.0
	c	6	37.0	10.0	99.0	68:51	98.0	65.0
	d	8	36.5	9.5	>100	64:11	84.0	70.0
C _{18:1} xvii	a	2	41.5	11.5	57.5	92:34	154	—
	b	4	38.5	10.5	65.0	85:12	147	40.0
	c	6	36.5	10.0	97.0	79:47	135	70.0
	d	8	34.0	8.5	99.0	73:23	103	80.0
C _{18:2} xviii	a	2	40.5	12.0	54.5	102:39	163	—
	b	4	38.5	10.0	78.0	93:51	145	20.0
	c	6	38.0	9.0	99.0	88:32	122	65.0
	d	8	35.0	6.5	>100	77:10	108	75.0
Mixed xix	a	2	44.0	11.5	58.5	105:11	199	—
	b	4	41.5	8.5	69.0	97:13	158	30.0
	c	6	38.5	7.5	89.0	91:28	137	60.0
	d	8	37.0	7.0	>100	89:42	111	80.0

3.1.1. Surface and interfacial tensions

Are characteristic for surface active compounds. It was found that, the disodium salts have pronounced surface activity (cf. Table V).

On the other hand, the propenoxyated α -palmitoyloxysuccinate recorded lower surface tension than all other prepared compounds. Generally the surface and interfacial tensions increased with increasing the number of propylene oxide unit cooperated with molecule. This leads to

decreasing in the surface activity. But the improvement of the surface activity was resulted by introducing amide oxime group (cf. Tables VI and VII).

3.1.2. Kraft point

Table V showed that, disodium salt recorded lower T_{kp} so, this compounds can be used at lower temperature.

3.1.3. Cloud Point

Was increased by increasing the number of propenoxy group per hydrophobic molecule. Also the amide oximes have cloud point higher than the corresponding propenoxyates (cf. Table VI and VII).

3.1.4. Wetting properties

The wetting time of amide oxime compound is very low than the corresponding propenoxyates. So the amide oxime (Table VI-VII) has benefit effect and was considered good wetting agents [19].

3.1.5. Foam height

The prepared propenoxyated compounds (v-ix)_{a-d} showed superior foaming ability to the corresponding amide oximes (xiv-xix)_{a-d} (cf. Tables VI, VII). A future of end -blocked nonionics is low foaming or antifoaming properties [20].

3.1.6. Emulsion stability

Studies are still being carried out on utilization of surfactants in emulsion formation which is immense importance to technological development. It was found that, emulsifying stability of the prepared surfactants especially those containing an amide oxime group has pronounced effect than that propenoxyated compounds [21]. At the same time, the emulsion stability decreased with increasing the number of propylene oxide units (cf. Tables VI-VII).

BIBLIOGRAPHY

1. El-Sukkary, M.M.A., El-Sawy, A.A. and F. El-Dib (1987).—«Synthetic detergents from crude rice bran oil».—*Hungarian Journal of Industrial Chemistry* **15**, 317.
2. Eissa A. M. F., Mahmoud A. A. and A. A. El-Sawy (1994).— «Preparation and surface active properties of oxypropylated diol monoesters of fatty acids with an amide oxime terminal group».—*Grasas y Aceites*, Vol. **(45)**, 306.
3. Eloy, F., and R. Lenaers (1962).—«The chemistry of amide oximes and related compounds».—*Chem. Rev.* **62**, 155.
4. Pearse, G. A. Jr. and R. T. Pflaum (1959).—«Interaction of metal ion with amide oxime».—*J. Am. Chem. Soc.* **81**, 6505.
5. Koide, Y., Takamoto, H., Matsukawa and Yamada (1983).—«Bull».—*Chem. Soc. Jpn.* **56**, 3364.
6. Jpn. Kokai 59-219422, Unitika Ltd., Dec. 10, (1984), pp. 123, (Chem. Abstracts 102: 13567u).
7. Masuyama, A., Tomomichi, O. and O. Mitsuo (1988).— «Preparation and surface active properties of alcohol ethoxylates with an amide oxime terminal group».—*J. Am. Oil Chemist's Soc.* **65**, 18.
8. El-Sawy, A. A. (1989).—«Synthesis of sucrose esters from rice bran oil fatty acids».—*Grasas y Aceites*, Vol. **(40)**, 382.
9. Youngs C. G., Epp A., Craig B. M. and H. R. Sallans (1955).—«Preparation of long- chain fatty acid chloride».—*J. Am. Oil Chem. Soc.* Vol **34**, 107.
10. Nakamura, M., Minami, N., Togo A. and W. Yano (1979).— «Synthesis and their surface activities of esters of hydroxy acid».—*Suzuka Kogyo Semmon Gakko Kiyō*, **12 (2)**, 247, (C.A., 92:60813 Japan).
11. El-Sawy, A.A., Mahomoud, A.A. and N.O. Shaker, (1990).—«Preparation and surface active properties of oxypropylated diol monoester of fatty acids».—*J. Serb. Chem. Soc.* **55 (7)**, 395.
12. Findly, A. (1963).—«Practical physical Chemistry».—*Longmans*, London, **6** th., Ed: 1040.
13. Wiel, J. K., Smith, F. D., Stirton, A. J. and R. G. Bistine, Jr. (1963).—«Long chain alkanesulphonates and 1-hydroxy- 2-alkanesulphonates: Structure and property relations».—*J. Am. Oil Chem. Soc.*, **40**, 538.
14. Durham, K., (1961).—«Surface activity and detergency».—*MacMillan & Co. Ltd.*, London.
15. Draves, C. Z. and R. Clarkso, (1931).—*J. Am. Dye Stuff Reporter*, **20**, 201.
16. Ross J., and G. D. Milles (1941).— «Oil and Soap».—**18**, 99.
17. Takeshi H. (1970).—«Studies of ester containing surfactant: Preparation and properties of sodium sulpho-alkanoates».—*Bull. Chem. Soc.*, **43**, 2236 (Japan).
18. Wilkes B.G. and J. N. Wiekert (1973).—*Ind. Eng. Chem.*, **22**, 1234.
19. Masuyama, A., Akiyama, K. and Okahara, M. (1987).— «Surface active hydroximic acids».—*J. Am. Oil Chem. Soc.* **64**:1040.
20. Mckenzie, D. A. and U. C., Corp (1978).—*J. Am. Oil Chem. Soc.*, **55**, 193.
21. Scholnick, F., Linfield, W. M., (1977).—«Lactose-derived surfactants (III): Fatty esters of oxyalkylated lactitol».—*J. Am. Oil Chem. Soc.* **54**, 430.

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