

Synthesis and surface active properties of cationic surface active agents from crude rice bran oil

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RESUMEN

Síntesis y propiedades tensioactivas de agentes tensioactivos catiónicos de aceite de germen de arroz crudo.

Se han preparado tensioactivos catiónicos de hidróxidos del 2-hidroxi-3-(2-alkilamidopoliethylamino) propano-1-triethylammonio (ix-xiii)_{a-d} a partir de los ácidos grasos (i)_{a-d} [ácido palmítico, esteárico, oleico y linoleico] y mezclas de ácidos grasos de aceite de germen de arroz crudo *i_e* [RBO]. La reacción de estos ácidos con etilendiamina, dietilendiamina, trietilendiamina y tetraetilendiamina (ii)_{a-d} produjo los compuestos (iii-vii)_{a-d}. Los amidopoliethylaminos producidos (iii-vii)_{a-d} reaccionaron con el cloruro de 2-epoxypropilendiammonio (viii) para dar los tensioactivos catiónicos (ix-xiii)_{a-d}. Los derivados producidos se purificaron y caracterizaron por microanálisis, determinación del peso molecular, espectros de infrarrojo (IR) y resonancia magnética nuclear de protón (¹H NMR). Se determinaron las propiedades tensioactivas y la eficacia de inhibición de los tensioactivos catiónicos preparados.

PALABRAS-CLAVE: Aceite de germen de arroz crudo - Propiedades tensioactivas - Síntesis - Tensioactivo catiónico.

SUMMARY

Synthesis and surface active properties of cationic surface active agents from crude rice bran oil.

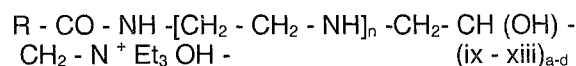
Cationic surfactants of 2-hydroxy-3-(2-alkylamidopolyethyl amino) propane-1-triethylammonium hydroxides (ix-xiii)_{a-d} were prepared from fatty acids (i)_{a-d} [palmitic, stearic, oleic, linoleic acid] and mixed fatty acids of crude rice bran oil *i_e* [RBO]. The reaction of these acids with ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine (ii)_{a-d} produced (iii-vii)_{a-d}. The produced amidopolyethylamine (iii-vii)_{a-d} reacted with 2-epoxypropylenetriethylammonium chloride (viii) to give the cationic surfactants (ix-xiii)_{a-d}. The produced derivatives were purified and characterized by microanalysis, molecular weight determination, infra-red (IR), and proton nuclear magnetic resonance (¹H NMR) spectra. The surface active properties and inhibition efficiency of the prepared cationic surfactants were determined.

KEY-WORDS: Cationic surfactant - Crude rice bran oil - Surface active properties - Synthesis.

1. INTRODUCTION

It has been reported that cationic surfactants, especially those having quaternary ammonium

groups, display an important role in the textile industry. They have antimicrobial activities and emulsifying properties in addition to their anticorrosive effects (1-8). These facts encouraged us to prepare a series of novel groups of cationic surfactants from the mixed fatty acids of Egyptian crude rice bran oil, which expected to have good emulsifying properties in nonedible medium as insecticides, and pesticides. The prepared surface active agent has the following formula.



R -	n
CH ₃ - (CH ₂) ₁₄ - (palmitic)	1
CH ₃ - (CH ₂) ₁₆ - (stearic)	2
CH ₃ - (CH ₂) ₇ - CH = CH - (CH ₂) ₇ - (oleic)	3
CH ₃ - (CH ₂) ₄ - CH = CH - CH ₂ - CH = CH - (CH ₂) ₇ - (linoleic)	4
Mixed alkyl of rice bran fatty acid composition.	

The structure of these compounds was based on the presence of hydrophobic part (fatty acids of rice bran oil) and hydrophilic part (quaternary ammonium moiety, amidopolyethylamine in addition to hydroxyl groups).

2. MATERIAL AND METHODS

All melting points are uncorrected; microanalysis and molecular weight determination by osmometric method, using CHCl₃ as solvent; IR spectrum were measured by a **Pye Unicam SR-1000** infrared spectrophotometer as Nujol mul and ¹H NMR spectra on a **Varian EM-390** spectrophotometer operating at 90 MHz, using (CD₃)₂ CO as solvent and tetramethylsilane (TMS) as internal standard have been done.

2.1. Crude Rice Bran Oil

The oil was supplied by the **Alexandria** company for extraction and hydrogenation of oils. The specifications are given in (Table I).

Table I
Specification of crude rice bran oil

Saponification value	179
Iodine value	108
Acid value	68

2.2. Hydrolysis of Crude Rice Bran Oil

The procedure described by **El-Sawy** (9) was followed. The fatty acid mixture was analysed by G.L.C and its composition is given in (Table II).

Table II
Fatty acids composition of rice bran oil

Acid	Peak area %
Saturated fatty acids	
Palmitic	17.6
Stearic	00.9
Unsaturated fatty acids	
Oleic	50.1
Linoleic	27.1
Linolenic	02.2

The oleic acid is the main constituent of mixed fatty acids of RBO; the molecular weight is considered as oleic acid_(M. Wt = 282).

2.3. N-Acylamidopolyethylamino Derivatives (iii-vii)_{a-d}

N-Pentadecyl-, heptadecyl-, heptadec-9-enyl-, heptadec-9, 12-dienyl and mixed acyl of RBO fatty acids amidopolyethylamino derivatives (iii-vii)_{a-d} were prepared by condensation of equimolar amounts of the corresponding pure fatty acid (palmitic, stearic, oleic and linoleic acid) or mixed fatty acids from rice bran oil with ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine (ii)_{a-d}. The reaction mixture was heated at 140 °C for 10 hours. The liberated theoretical amount of water was collected to ensure the reaction completion, by using **Dean and Stark** apparatus and benzene as solvent. The organic solvent was removed under reduced pressure, and the residue was recrystallized from isopropanol. The yields, melting points, and elemental analysis were used to identify the obtained compounds and collected in Table III.

2.4. 2,3-Epoxypropyl triethylammonium Chloride (viii)

A mixture of (9.25 g, 0.1 mole) epichlorohydrin and (10.19 g, 0.1 mole) triethylamine in 10 ml of distilled water was stirred at room temperature for about 5.5 hours. The resulting clear solution which consists mainly of compound (viii) was used directly in the next step without further purification (10).

2.5. Conversion of the Prepared N-acylamidopolyethylamino Derivatives to Cationic Surfactants (ix-xiii)_{a-d}

A mixture of (0.1 mol.) from the fatty amidopolyethylamino derivatives (iii-vii)_{a-d} and an adequate amount of 2,3-epoxypropylammonium chloride (viii) in 100 ml dry benzene, was stirred under reflux for about 24 hours. The solvent was evaporated, and the remaining waxy residue was thoroughly extracted with hot distilled water till no froth persisted. The aqueous extract was subjected to high speed centrifugation (10⁴ rpm) for 15 min to remove the suspended particles of the unreacted matter. The supernatant clear aqueous layer was decanted, shaken with pet. ether (40-60 °C) to remove the residual unreacted matter, and rendered alkaline with 10 % sodium hydroxide solution. The product was extracted three times each with 50 ml portions of isoamyl alcohol (11). The solvent was evaporated on a boiling water-bath under vacuum to leave a pale yellow waxy residue (cf. scheme 1). Elemental analysis; molecular weight determination, IR and ¹H NMR spectroscopic analysis were conducted to confirm the structure of some examples of the prepared compounds (cf. Tables IV-V).

2.6. Evaluation of the Surface Active Properties of the Prepared Cationic Surfactants

2.6.1. Surface and interfacial tensions, were measured using a **Du-Nouy** tensiometer (12) [Kruss, Type 8451] with 0.1 wt% aqueous solution at room temperature 25 °C.

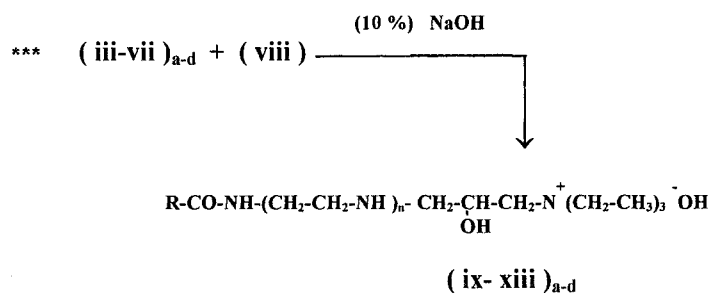
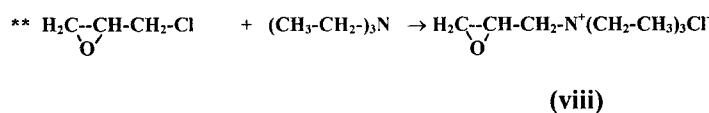
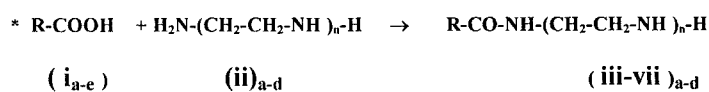
2.6.2. Kraft point, of the prepared surfactants, were measured as the temperature at which 1% dispersion becomes clear on gradual heating (13).

2.6.3. Cloud point, was determined by gradually heating 1 wt% solution in controlled temperature bath and recoding the 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).

Table III
Elemental analysis of N-acylamido polyethylamino derivatives (iii-vii)_{a-d} R - CO - NH - (CH₂ - CH₂ - NH)_n - H

Compd. no.	n	R	m.p °C	Yield %	Mol. formula	Mol. Wt	C %		H %		N %		
							Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	
iii	a	1	CH ₃ (CH ₂) ₁₄ -	147 - 48	67	C ₁₉ H ₃₈ N ₂ O	298	72.48	72.1	12.75	12.6	9.39	9.2
	b	2	" " "	153 - 54	82	C ₂₀ H ₄₃ N ₃ O	341	70.38	70.0	12.60	12.4	12.31	12.1
	c	3	" " "	158 - 60	79	C ₂₂ H ₄₈ N ₄ O	384	68.75	68.6	12.50	12.2	14.58	14.3
	d	4	" " "	164 - 66	74	C ₂₄ H ₅₃ N ₅ O	427	67.44	67.3	12.41	11.9	16.39	16.0
iv	a	1	CH ₃ (CH ₂) ₁₆ -	151 - 53	72	C ₂₀ H ₄₂ N ₂ O	341	70.38	70.2	12.31	12.2	8.21	8.0
	b	2	" " "	158 - 59	76	C ₂₂ H ₄₇ N ₃ O	384	68.75	68.0	12.23	12.1	10.93	9.7
	c	3	" " "	162 - 64	81	C ₂₄ H ₅₂ N ₄ O	427	67.44	67.1	12.17	12.1	13.11	13.1
	d	4	" " "	167 - 69	73	C ₂₆ H ₅₇ N ₅ O	470	66.38	65.8	12.12	11.7	14.89	13.8
v	a	1	CH ₃ (CH ₂) ₇ - CH = CH - (CH ₂) ₇ -	63 - 65	63	C ₂₀ H ₄₀ N ₂ O	339	70.79	69.7	11.79	11.0	8.25	8.0
	b	2	" " " "	67 - 68	67	C ₂₂ H ₄₅ N ₃ O	382	69.10	68.1	11.78	10.9	10.99	9.8
	c	3	" " " "	69 - 71	79	C ₂₄ H ₅₀ N ₄ O	425	67.79	66.3	11.76	10.5	13.17	13.8
	d	4	" " " "	77 - 79	69	C ₂₆ H ₅₅ N ₅ O	468	66.66	65.3	11.36	10.0	15.11	14.8
vi	a	1	CH ₃ (CH ₂) ₄ - CH = CH - CH ₂ - CH = CH - (CH ₂) ₇ -	40 - 41	82	C ₂₀ H ₄₀ N ₂ O	337	71.21	69.5	11.26	10.5	8.3	13.8
	b	2	" " " " " "	46 - 48	79	C ₂₂ H ₄₃ N ₃ O	380	69.94	68.1	11.31	11.1	11.05	11.0
	c	3	" " " " " "	49 - 51	81	C ₂₄ H ₄₉ N ₄ O	423	68.80	67.6	11.11	10.8	13.23	13.1
	d	4	" " " " " "	53 - 55	69	C ₂₆ H ₅₃ N ₅ O	466	66.95	65.0	11.36	10.7	15.05	14.3
vii	a	1	Mixed alkyl chain of rice bran fatty acids	*	84	*	*	*	69.0	*	11.4	*	9.4
	b	2	" " " " " " " "	*	83	*	*	67.3	*	11.0	*	10.4	
	c	3	" " " " " " " "	*	79	*	*	65.5	*	10.5	*	11.9	
	d	4	" " " " " " " "	*	82	*	*	64.9	*	10.3	*	14.4	

* Not calculated because is the mixed fatty acids composition of crude rice bran oil.



Where:

i _a , iii _{a-d} and ix _{a-d}	R =	CH ₃ -(CH ₂) ₁₄ -	;	(n=1,2,3 and 4)
ib, iv _{a-d} and x _{a-d}	R =	CH ₃ -(CH ₂) ₁₆	;	"
ic, v _{a-d} and xi _{a-d}	R =	CH ₃ -(CH ₂) ₇ -CH=CH-(CH ₂) ₇ -	;	"
id, vi _{a-d} and xii _{a-d}	R =	CH ₃ -(CH ₂) ₄ -CH=CH-CH ₂ -CH=CH-(CH ₂) ₇ -	;	"
iv, vii _{a-d} and xiii _{a-d}	R =	Mixed alkyl of fatty acids composition of rice bran oil;	;	"

Scheme 1

Table IV
Elemental analysis of the prepared surfactants (ix - xiii)_{a-d}
R - CO - NH (-CH₂ - CH₂ NH)_n CH₂ - CH (OH) - CH₂ - N⁺Et₃⁻ OH

Compd. no.	n	R	m.p °C	Yield %	Mol. formula	Mol. Wt **		C%		H%		N%		
						Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	
ix	a	1	CH ₃ (CH ₂) ₁₄ -	waxy	28	C ₂₇ H ₅₉ N ₃ O ₃ ·2H ₂ O	509	500	63.65	62.1	12.37	12.0	8.25	8.4
	b	2	" " "	waxy	22	C ₂₉ H ₆₄ N ₃ O ₃ ·2H ₂ O	552	568	63.3	63.0	11.59	11.4	10.15	10.1
	c	3	" " "	waxy	28	C ₃₁ H ₆₉ N ₃ O ₃ ·2H ₂ O	595	540	62.52	61.6	11.59	11.2	11.76	10.6
	d	4	" " "	visc. oil	27	C ₃₃ H ₇₄ N ₃ O ₃ ·2H ₂ O	638	630	62.06	61.9	11.60	11.0	13.16	13.0
x	a	1	CH ₃ (CH ₂) ₁₆ -	waxy	27	C ₂₉ H ₆₃ N ₃ O ₃ ·2H ₂ O	537	528	64.8	64.0	12.19	12.2	7.82	8.0
	b	2	" " "	waxy	29	C ₃₁ H ₆₈ N ₃ O ₃ ·2H ₂ O	580	570	64.13	63.9	11.68	12.1	9.65	9.3
	c	3	" " "	waxy	32	C ₃₃ H ₇₃ N ₃ O ₃ ·2H ₂ O	623	620	63.56	62.8	11.70	12.1	11.25	10.1
	d	4	" " "	waxy	30	C ₃₅ H ₇₈ N ₃ O ₃ ·2H ₂ O	666	645	63.06	62.0	11.70	11.7	12.61	12.8
xi	a	1	CH ₃ (CH ₂) ₇ - CH = CH - (CH ₂) ₇	visc. oil	23	C ₂₉ H ₅₁ N ₃ O ₃ ·2H ₂ O	535	536	65.04	64.7	11.40	11.0	7.85	8.0
	b	2	" " " "	visc. oil	21	C ₃₁ H ₅₆ N ₃ O ₃ ·2H ₂ O	580	570	64.35	64.3	11.41	10.9	9.68	9.1
	c	3	" " " "	visc. oil	29	C ₃₃ H ₇₁ N ₃ O ₃ ·2H ₂ O	621	612	63.76	62.1	11.43	10.5	11.27	11.0
	d	4	" " " "	visc. oil	26	C ₃₅ H ₇₆ N ₃ O ₃ ·2H ₂ O	664	654	63.25	63.0	11.44	10.0	12.65	12.1
xii	a	1	CH ₃ (CH ₂) ₄ - CH = CH - CH ₂ - CH = CH (CH ₂) ₇	visc. oil	25	C ₂₉ H ₅₉ N ₃ O ₃ ·2H ₂ O	533	510	65.29	63.4	11.81	10.9	7.87	7.9
	b	2	" " " " " "	visc. oil	26	C ₃₁ H ₆₄ N ₃ O ₃ ·2H ₂ O	576	546	64.58	63.5	12.15	11.9	9.72	8.9
	c	3	" " " " " "	visc. oil	20	C ₃₃ H ₆₉ N ₃ O ₃ ·2H ₂ O	619	593	63.97	61.8	11.79	11.8	11.30	10.9
	d	4	" " " " " "	visc. oil	28	C ₃₅ H ₇₄ N ₃ O ₃ ·2H ₂ O	662	618	63.44	62.1	11.78	10.0	12.68	12.3
xiii	a	1	Mixed alkyl chain of rice bran fatty acids	waxy	29	*	*	*	*	64.4	*	11.9	*	8.3
	b	2	" " " " " "	waxy	31	*	*	*	*	55.9	*	11.0	*	9.4
	c	3	" " " " " "	waxy	29	*	*	*	*	63.2	*	10.6	*	10.9
	d	4	" " " " " "	visc. oil	34	*	*	*	*	61.4	*	10.7	*	11.4

* Not calculated because is the mixed fatty acids composition of crude rice bran oil.

** Allowable error of the mol. weight determination by osmometric method is 10%.

Table V
Spectral data of some examples from the prepared surfactants
R - CO - NH (-CH₂ - CH₂ NH)_n- CH₂ - CH (OH) - CH₂ - N⁺Et₃⁻ OH.

Compound no.	¹ H NMR (δ = ppm)	IR (cm ⁻¹)
ix a	δ 0.8 (t,3H, term. CH ₃); δ 0.9 (br. s.; 26H, CH ₂ chain); δ 1.5 (br.t, 2H, CH ₂ CO-); δ 2.0 -2.2 (br.s; 6H, -NH CH ₂ CH ₂ -NH -CH ₂ -); δ 2.6 (t, 9H, N (-CH ₂ -CH ₃) ₃); δ 3.9 (m; 8H, CH ₂ N (-CH ₂ -CH ₃) ₃ ; δ 4.0 (br.s, 1H; OH); and δ 7.9 (s.; 1H, ionized OH).	3350-3200 cm ⁻¹ v NH; 3500-3400 cm ⁻¹ v OH; 1650-1560 cm ⁻¹ v CO of amide and broad band at; 2050-2200 cm ⁻¹ for v CH ₂ N ⁺ (-CH ₂ - CH ₃) ₃ .
ix b	δ 0.9 (t,3H, term. CH ₃); δ 1.2 (br. s.; 26H, CH ₂ chain); δ 1.25 (br.t, 2H, CH ₂ CO-); δ 1.3-1.4 (br.s; 10H, -NH CH ₂ CH ₂ -NH -CH ₂ -CH ₂ -NH-CH ₂ -); δ 2.8 (t; 9H, N (-CH ₂ -CH ₃) ₃); δ 3.7 (m; 8H, CH ₂ N (-CH ₂ -CH ₃) ₃ ; and δ 4.0 (br.s, 1H; OH).	3400-3500 cm ⁻¹ v OH; 3350-3200 cm ⁻¹ v NH; 1560 cm ⁻¹ v CO of amide; 2100 cm ⁻¹ for v -CH ₂ N ⁺ (-CH ₂ - CH ₃) ₃ .
x a	δ 0.7 (t,3H, term. CH ₃); δ 0.9 (br. s.; 30H, CH ₂ chain); δ 1.5 (br.t, 2H, CH ₂ CO-); δ 2.0 -2.2 (br.s; 6H, -NH -CH ₂ -CH ₂ -NH -CH ₂ -); δ 2.6 (t, 9H, N (-CH ₂ -CH ₃) ₃); δ 3.9 (m; 8H, CH ₂ N (-CH ₂ -CH ₃) ₃ ; δ 4.0 (br.s, 1H; OH); and δ 7.9 (s.; 1H; OH).	3400-3500 cm ⁻¹ v OH; 3350-3200 cm ⁻¹ v NH; 1650 cm ⁻¹ v C = C of oleic chain 1580 cm ⁻¹ v CO of amide 2080 cm ⁻¹ for v CH ₂ N ⁺ (-CH ₂ - CH ₃) ₃ .
xi a	δ 0.85 (t,3H, term. CH ₃); δ 0.9 (br.s.; 26H, CH ₂ chain); δ 1.5 (br.t, 2H, CH ₂ CO-); δ 2.0 -2.2 (br.s; 6H, -NH -CH ₂ -CH ₂ -NH -CH ₂ -); δ 2.6 (t, 9H, N (-CH ₂ -CH ₃) ₃); δ 3.9 (m; 8H, CH ₂ N (-CH ₂ -CH ₃) ₃ ; δ 4.0 (br.s, 1H, OH); δ 5.3 -5.5 (br.s, 2H, -CH = CH-) and δ 7.9 (s., 1H, ionized OH).	*****
xii a	δ 0.9 (t,3H, term. CH ₃); δ 1.1 (br.s.; 20H, CH ₂ chain); δ 1.5 (br.s., 2H, CH ₂ CO-); δ 1.8 -2.1 (br.s.; 6H, -NH -CH ₂ -CH ₂ -NH -CH ₂ -); δ 2.6 (t, 9H, N (-CH ₂ -CH ₃) ₃); δ 3.2 - 3.6 (m; 8H, CH ₂ N (-CH ₂ -CH ₃) ₃ ; 4.0 (br.s.; 1H, OH); δ 5.2 - 5.4 (br.s.; 4H, -CH = CH - CH ₂ - CH = CH-) and δ 7.9 (s.; 1H, ionized OH).	3400-3500 cm ⁻¹ v OH; 3350-3200 cm ⁻¹ v NH; 3100 cm ⁻¹ v CH - olifinic; 1650 cm ⁻¹ v C = C of oleic chain 1580 cm ⁻¹ v CO of amid 2100 cm ⁻¹ for CH ₂ N ⁺ (-CH ₂ - CH ₃) ₃ .
xiii a	δ 0.9 (t,3H, term. CH ₃); δ 1.1 (br.s.; CH ₂ chain); 1.4 (br.s., 2H, CH ₂ CO-); δ 1.9 - 2.2 (br.s.; 6H, -NH CH ₂ CH ₂ -NH -CH ₂ -); δ 2.7 (t, 9H, N (-CH ₂ -CH ₃) ₃); δ 3.2 - 3.6 (m; 8H, CH ₂ N (-CH ₂ -CH ₃) ₃ ; δ 4.0 (br.s.; 1H, OH); δ 5.2 - 5.4 (br.s, -olifinic protons) and δ 7.9 (s.; 1H, ionized OH).	3400-3500 cm ⁻¹ v OH; 3350-3200 cm ⁻¹ v NH; 3100 cm ⁻¹ v CH - olifinic; 1650 cm ⁻¹ v C = C of unsaturated fatty chain; 1560 cm ⁻¹ v CO of amid 2080 cm ⁻¹ for CH ₂ N ⁺ (-CH ₂ - CH ₃) ₃ .

2.6.4. Wetting time, was determined by immersing a sample of cotton fabric in 0.1 wt% aqueous solution of the surfactants (15).

2.6.5. Foaming properties, were measured by Ross Miles (16) method. The foam production for 0.1 wt% solution was measured by the foam height initially produced.

2.6.6. Emulsion stability: The emulsion was prepared from 10 ml. of a 20 m mole aqueous solution of surfactant and 5 ml of toluene at 40 °C. The emulsifying property was determined by the time it took for an aqueous volume separating from the emulsion layer to reach 9 ml counting from the moment of the cession shaking (17).

2.6.7 Stability to hydrolysis: a mixture of 10 m mole surfactant and 10 ml 2 N H₂SO₄ or 0.05 N NaOH were placed in a 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 (18).

2.7. Inhibition Efficiency

The effect of increasing concentrations for some prepared cationic surfactants as corrosion inhibitors for dissolution of carbon steel (Type 5 Px -L) was studied using weight loss technique (19). The chemical composition of carbon steel 0.26% C, 1.35% Mn, 0.09% P, 0.05% S, 0.005 Nb, 0.02% V, 0.03% Ti and the remainder is iron. Carbon-steel compositions measuring 10 x 20 x 3 mm were used. The specimen was immersed in 100ml of test solution for period of 6 hours at room temperature.

The percent of inhibition efficiency (I.E) was calculated from the following equation:

$$I.E = 100 [1 - (W_{add} / W_{free})]$$

Where: W_{add} and W_{free} are the weight loss of steel in presence and in absence of the inhibitor.

3. RESULTS AND DISCUSSION

Preparation of cationic surfactants (ix-xiii)_{a-d} was easy and could be isolated in suitable yield (cf. Tables III-IV); 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 V).

3.1. Surface and interfacial tension: Cationic surfactants prepared from unsaturated acids (xi-xii)_{a-d} recorded higher surface and interfacial tension than those prepared from saturated fatty acids (ix-x)_{a-d} (cf. Tables VI-VII); while surfactants obtained from mixed fatty acids of crude rice bran oil recorded almost the same surface and interfacial tension as those prepared from individual commercial unsaturated fatty acid (cf. Table VIII). Also, it was noted that as the ethylamino unit increased the surface and interfacial tension decreased; it is may be attributed to increasing the hydrophilicity of the molecules, leading to increase solvation due to hydrogen bonding.

Table VI
Surface properties of the prepared surfactants (ix-x)_{a-d}
R - CO - NH (-CH₂ - CH₂ NH)_n - CH₂ - CH (OH) - CH₂ - NEt₃⁺ OH⁻

Compd. no.	S.T mN/m (0.1%)	I.F.T. mN/m (0.1%)	Cloud point °C (1%)	Wetting time (sec.) (0.1%)	Foam height (m.m.) (0.1%)	Emul. stability		Stability to hydrolysis		
						(min.)	(sec.)	Base		
						(min.)	(sec.)	(min.)	(sec.)	
C ₁₆	ix _a	42.5	9.5	—	68	205	234	40	498	13
	ix _b	41.0	8.0	95	62	250	372	43	681	29
	ix _c	38.0	7.5	> 100	35	350	401	37	710	36
	ix _d	36.5	5.0	> 100	28	510	518	53	772	32
C ₁₈	x _a	44.0	12	—	76	230	267	42	431	43
	x _b	43.5	9.0	91	68	260	391	29	630	56
	x _c	41.5	8.0	> 100	54	310	429	25	732	38
	x _d	39.0	6.5	> 100	47	480	543	19	787	20

Table VII
Surface properties of the prepared surfactants (ix-xii)_{a-d}
R - CO - NH (-CH₂ - CH₂ NH-)_n - CH₂ - CH (OH) - CH₂ - NET⁺₃ OH⁻

Compd. no.	S.T mN/m (0.1%)	I.F.T. mN/m (0.1%)	Cloud point °C (1%)	Wetting time (sec.) (0.1%)	Foam height (m.m.) (0.1%)	Emul. stability		Stability to hydrolysis		
						(min.)	(sec.)	Base		
						(min.)	(sec.)	(min.)	(sec.)	
Oleic	xia	46.0	13.0	—	50	160	372	40	516	31
	xib	43.0	12.0	85	47	350	486	43	572	10
	xic	42.0	9.0	95	41	650	543	37	590	00
	xid	39.0	8.0	> 100	33	800	612	53	599	23
Linoleic	xii _a	47.0	13.5	—	65	280	380	42	520	12
	xii _b	46.0	12.5	87	54	360	490	29	576	42
	xii _c	44.0	11.0	99	40	390	536	25	598	16
	xii _d	42.5	8.0	> 100	25	470	673	19	612	52

Table VIII
Surface properties of the mixed cationic surfactants prepared from rice bran oil (xiii)_{a-d}
R - CO - NH (-CH₂ - CH₂ NH-)_n - CH₂ - CH (OH) - CH₂ - NET⁺₃ OH⁻

Compd. no.	S.T mN/m (0.1%)	I.F.T. mN/m (0.1%)	Cloud point °C (1%)	Wetting time (sec.) (0.1%)	Foam height (m.m.) (0.1%)	Emul. stability		Stability to hydrolysis	
						(min.)	(sec.)	Base	
						(min.)	(sec.)	(min.)	(sec.)
xiii _a	50.0	13.5	—	35	290	370	40	473	58
xiii _b	48.0	12.0	> 100	28	350	395	43	498	45
xiii _c	43.5	8.5	> 100	20	420	412	37	513	33
xiii _d	40.5	6.0	> 100	10	530	501	53	521	39

3.2. Kraft and cloud points: All these cationic surfactants (ix-xiii)_{a-d} were readily soluble in water, and have excellent hydrophilicity for practical use because their kraft points (T_{kp}) were below 0 °C, and their high cloud point (cf. Tables VI-VIII); it is considered that, the remarkable decrease in (T_{kp}) and high cloud point for the prepared surfactants is attributed to the co-operative effect of quaternary ammonium moiety and repeating nitrogen linkages.

3.3. Foam height and wetting: It is reported that, the efficiency of surfactant as a foamer increases with increased alkyl chain length (20-21). In general the foam height and wetting time for the surfactants prepared from saturated fatty acids (ix-x)_{a-d} recorded more improving than those prepared from unsaturated acids (xi-xii)_{a-d}. On the other hand, cationic surfactants (xiii)_{a-d} prepared from mixed fatty acids of (RBO) revealed good wetting properties.

3.4. Emulsion stability: Studies are still being carried out on the utilization of surfactants in emulsion formation which is of immense importance to technological development. It was proved that the emulsifying stability of the prepared surfactants especially those of (RBO) exhibit good emulsifying properties (cf. Tables VI-VIII) which make them of choice in pesticide and cosmetic formulations.

3.5. Stability towards acid and base: Concerning to the stability towards acid and base hydrolysis, all the prepared surfactants have higher stability in acidic than in basic medium (cf. Tables VI-VIII); this may be due to the presence of free nitrogen atom which reacted with the acid forming more cationic centers (22).

3.6. Corrosion Inhibition: This was done by using weight loss technique. Table (IX) shows that the effect of increasing concentrations of the prepared

cationic surfactants (as example x_d , $xiii_d$) on corrosion of carbon steel specimen in 3.5% NaCl as corrosion medium. It reveals that, the weight loss decreases as the concentration of the tested examples increases and hence increases the value of inhibition efficiency. Also, it was found that, the cationic surfactant prepared from mixed fatty acids of rice bran oil ($xiii_d$) recorded higher inhibition efficiency than (x_d). These effected was attributed to their adsorption and the formation of a barrier film on the metal surface (23).

Table IX
Effect of increasing concentrations of cationic surfactants on the weight loss of carbon steel in 3.5% NaCl solution

Inhibition concentration (ppm)	Weight loss ($mg\ dm^{-2}$)	Inhibition efficiency
x_d • 00.00	850	—
10.00	640	24.70
50.00	560	34.11
100.00	512	39.76
200.00	435	48.82
300.00	315	62.94
500.00	105	87.64
$xiii_d$ • 00.00	850	—
10.00	614	27.76
50.00	535	37.05
100.00	466	45.17
200.00	395	53.52
300.00	285	66.47
500.00	98	88.47

4. CONCLUSION

From the previous results, may conclude that: All the prepared cationic surfactants have good surface properties, and they could be used as good emulsifier in non edible medium as insecticides, pesticides and also as corrosion inhibitors. The local non edible crude rice bran oil can be used as raw material for preparing these surfactants.

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