

This article was downloaded by: [Eindhoven Technical University]

On: 21 November 2014, At: 03:47

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Dispersion Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/Idis20>

Synthesis and Evaluation of Anionic Copolymeric Surfactant as Dispersing Agent for Some Heterocyclic Azo-Dyes

W. I. A. El-DougDoug^a

^a Chemistry Department , Faculty of Science, Benha University , Benha, Egypt

Published online: 17 Sep 2010.

To cite this article: W. I. A. El-DougDoug (2010) Synthesis and Evaluation of Anionic Copolymeric Surfactant as Dispersing Agent for Some Heterocyclic Azo-Dyes, Journal of Dispersion Science and Technology, 31:10, 1298-1306, DOI: [10.1080/01932691.2010.506848](https://doi.org/10.1080/01932691.2010.506848)

To link to this article: <http://dx.doi.org/10.1080/01932691.2010.506848>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synthesis and Evaluation of Anionic Copolymeric Surfactant as Dispersing Agent for Some Heterocyclic Azo-Dyes

W. I. A. El-DougDoug

Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

Series of polymeric surfactants based on decylacrylate (M_1) as hydrophobe and oxypropylated maleate ($M_{2,4,6}$ and 8 with different molar ratios of propylene oxide) as hydrophiles were prepared by copolymerization in presence of 1mole% azobisisobutyronitrile (AIBN) as free radical initiator to afford $[PMm_2, PMm_4, PMm_6, \text{ and } PMm_8]_{a-i}$. The reaction mixtures were followed by sulfation and neutralization to attain $[PMmS_2, PMmS_4, PMmS_6, \text{ and } PMmS_8]_{a-i}$ as anionic copolymeric surfactants, in good yield. These derivatives were purified and characterized by microanalysis, infrared, and 1H -NMR spectra studies. Also, surface activity, dispersing properties, and biodegradability were evaluated. The prepared anionic copolymeric surface active agents revealed good surface activities and high dispersing properties above 70% special for $PMmS_8$ with 8 mole propylene oxide and equal molar ratio from hydrophilic and hydrophobic monomers. Also, they are more biodegradable than traditional surfactants.

Keywords Copolymerization, decylacrylate ester, dispersing properties, oxypropylation, surface activity

INTRODUCTION

Surface active polymers, or polymeric surfactants, have gained great extent during the last two decades. These surfactants are now used commercially in many different applications, for example, stabilization of dispersion is probably the most widespread. Many water-soluble polymers, because of their amphipathic structure and surface activity similar to the traditional surfactants, are used as surfactants for example, the lignosulfonates exhibit excellent dispersant properties in disperse or vat dye systems.^[1–3]

The polysorbates exhibit excellent emulsifying properties for oil-in-water systems.^[4,5] On the other hand, propylene oxide-ethylene oxides block copolymers used as demulsifiers for water-oil emulsions.^[6] Also, other types exhibit good dispersing and emulsions stabilization.^[7] However, limited information's are available regarding water-soluble polyesters as surfactants in polymers that have an amphipathic molecular structures similar to traditional surfactants.^[8,9] Various types of surface active agents will perform the

dispersing present in commercial disperse dye powders may be regarded as the vehicle dye proper travels from the dispersing plant of the dye factory to the textile fiber being dyed.^[10] More widely used today are the condensation products of naphthalene sulfonic acid and formaldehyde, which are powerful dispersing agents.^[11]

Author aims to prepare a series of copolymeric surfactants as primary step for the utilization of long chain fatty alcohols obtained from vegetable seeds waste to synthesized such useful compounds in this field as the previous works^[12–14] (Scheme 1). Also, studies the surface active properties, biodegradability, and dispersion properties for commercial dispersed dye (Rhodanine azo-dye (A_{1-3}) and Antipyrine azo-dye (B_{1-4})) were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Acrylic acid, propylene oxide, maleic acid, n-decyl alcohol, *p*-toluene sulfonic acid, chlorosulfonic acid, sodium hydroxide, and potassium hydroxide were purchased from Merck (USA). Azobisisobutyronitrile (AIBN) was obtained from Aldrich (USA).

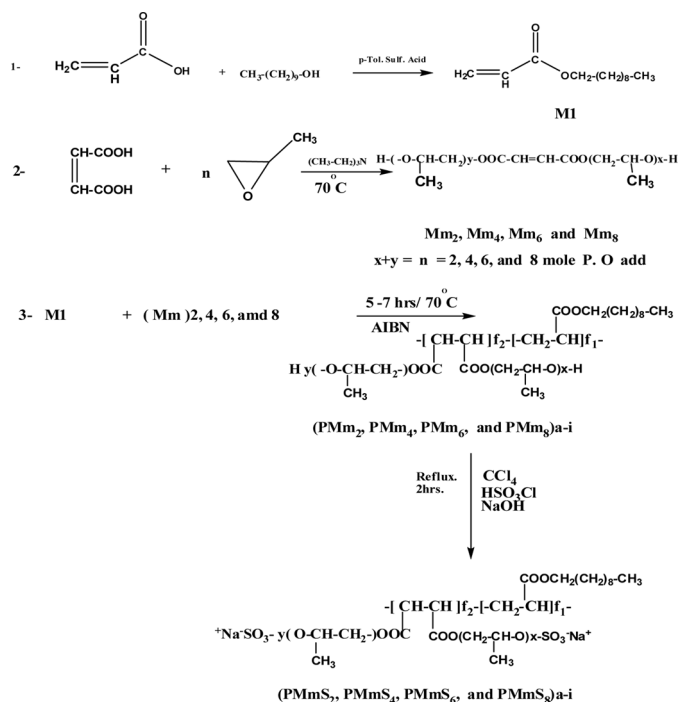
2.2. Methods

The infrared absorption spectra were determined with a "PYE UNICAM LTD" spectrophotometer using KBr pellet wafer technique. H-NMR data were recorded on a

Received 15 March 2009; accepted 16 April 2009.

The author is currently affiliated with Chemistry Department, Teachers College, Umm Al-Qura University, Makkah El-Mukarramah, Saudi Arabia.

Address correspondence to W. I. A. El-DougDoug, Chemistry Department, Universal College, Umm Al-Qura University, P.O. Box 2064, 00966, Makkah El-Mukarramah, Saudi Arabia. E-mail: eldougDoug@yahoo.com



Where:- (PMmS₂, PMmS₄, PMmS₆, and PMmS₈)_{a-i}

a: f1=0.9, f2=0.1	d: f1=0.8, f2=0.2	g: f1=0.8, f2=0.2
b: f1=0.8, f2=0.2	e: f1=0.8, f2=0.2	h: f1=0.8, f2=0.2
c: f1=0.8, f2=0.2	f: f1=0.8, f2=0.2	i: f1=0.8, f2=0.2

SCH. 1.

Varian instrument division EM-(360/390) PMR spectrometer, (CDCl₃-DMSO-d₆) and/or chemical shifts are reported in ppm (δ) relative to internal TMS. Microanalytical data were performed at MicroAnalytical Center at Cairo University, Egypt.

Decylacrylate Ester (M₁): Acrylic acid was esterified with n-decyl alcohol using Dean and Stark adapter in dry benzene as solvent and *p*-toluene sulfonic acid as catalyst to afford n-decylacrylate as hydrophobic monomer (M₁) in good yield.^[14,15]

Oxypropenylation of Maleic Acid: Interaction of maleic acid, propylene oxide and triethylamine as catalyst was conducted at 60°C for about 8 hours as described by El-Sawy.^[16]

Copolymerization Reactions: Binary copolymers from M₁ with Mm₂, Mm₄, Mm₆, and/or Mm₈ were obtained by solution polymerization in DMF (1.5 mol/l) at 65°C, in the presence of 1 mol% AIBN based on total monomer, according to the method previously described^[17,18]. The predetermined amounts of the monomers (M₁ and Mm₂, Mm₄, Mm₆, and/or Mm₈) were placed in polymerization tubes and diluted with dimethylformamide (DMF). Total monomers concentration was 2 mol/l. Polymerization was initiated by adding 1 mole% azobisisobutyronitrile (AIBN) as a free radical initiator. Tubes were flushed with nitrogen

gas for about 20 minutes then sealed and kept at 65°C for 15–30 hours, depending on the monomer pairs and composition. Copolymers were obtained by reprecipitation from petroleum ether (40–60°C) and finally dried under vacuum at 60°C to give [PMm₂, PMm₄, PMm₆, and PMm₈]_{a-i}.

Sulfation of Copolymeric Derivatives: The procedure illustrated by El-Sawy,^[13] was followed to afford [PMmS₂, PMmS₄, PMmS₆, and/or PMmS₈]_{a-i} with *n* = 2, 4, 6, and 8 of propylene oxide, respectively.

Surface Properties

Surface and interfacial tensions were measured using a Du-Nouy tensiometer^[19] (Kruss, Type 8451), with 0.1% aqueous solution at room temperature (25°C).

Kraft point was measured as the temperature at which 1% dispersion solution becomes clear on gradual heating.^[20]

Wetting time was determined by immersing a sample of cotton fabric in 0.1% aqueous solution of the surfactants.^[21]

Foaming properties were measured according to Ross and Miles method.^[22] The foam production for 0.1% solution was measured by the foam height initially produced.

For the emulsion stability, the emulsion was prepared from 10 ml of 20 mmol 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.^[23]

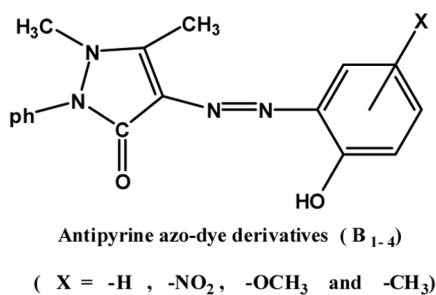
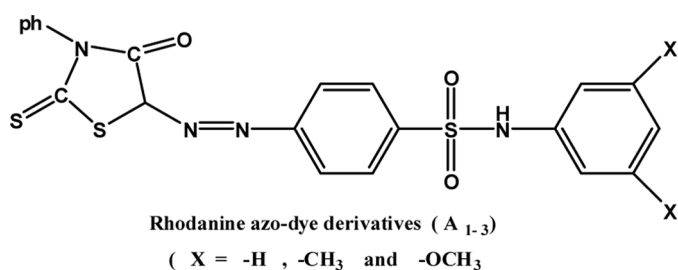
To determine the stability to hydrolysis, a mixture of 10 mmol polymeric surfactant and 10 ml 0.05 N NaOH were placed in a thermostat at 40°C. The time required for a sample solution to be clouded as a result of hydrolysis shows the stability of surfactant to hydrolysis.^[24]

Ca²⁺ stability was determined by a modified Hart method where, the surfactant (10 mmol) solution was titrated against CaCl₂ solution (0.1 N). The end point was determined by visual observed of cloudiness the surfactant solution.^[25]

Dispersing properties were determined by the following method: 100 ml solution of 0.1 gm of commercial dispersed dye (Rhodanine azo-dye (A₁₋₃) or antipyrine azo-dye (B₁₋₄)) (Scheme 2) and 0.1 gm of the dispersing agent was adjusted at pH = 7.5 using acetic acid.^[26,27] Then, the solution was heated to 130°C by a computer-controlled dyeing system under pressure for 1 hour then cooled to 90–95°C and vacuum-filtered immediately with a bunchner funnel. The filtrate was determined spectrophotometrically and the dispersability was calculated as follows:

Dispersability %

$$= \frac{\text{Dye concentration of filtrate}}{\text{Dye concentration of the original soln.}} \times 100$$



SCH. 2.

Biodegradability Percentage

Biodegradation is carried out by bacteria in nature. By enzymatic reactions, a surfactant molecule is ultimately converted into carbon dioxide, water and oxides of the other elements. If the surfactant does not undergo natural biodegradation then it is stable and persists in the environment. For surfactants the rate of biodegradation varies from 1–2 hours for fatty acids, 1–2 days for linear alkyl benzene sulfonates and several months for branched alkyl benzene sulfonates. The rate of biodegradation depends on the surfactant concentration, pH, and temperature. The temperature effect is particularly important, since the rate can vary by as much a factor of five between summer and winter in Northern Europe. Two criteria are important when testing for biodegradation: (1) primary degradation that results in loss of surface activity and (2) ultimate biodegradation, i.e., conversion into carbon dioxide, which

can be measured using closed bottle tests. The rate of biodegradation also depends on the surfactant structure. For example, the surfactant must be water soluble. Biodegradability percentage was determined following the method of Eter,^[28] according to the following equation:

$$D\% = \left[\frac{\gamma_t - \gamma_0}{\gamma_{bt} - \gamma_0} \right] \times 100$$

where: γ_t = surface tension at time t, γ_0 = surface tension at time zero; γ_{bt} = surface tension of blank at time t, without sample.

3. RESULTS AND DISCUSSION

The preparation of anionic copolymeric surfactants [PMmS₂, PMmS₄, PMmS₆, and/or PMmS₈]_{a-i} was performed giving suitable yields. Microanalysis of monomers; infrared (IR), and proton nuclear magnetic resonance (¹H-NMR) spectra; were carried out to confirm the structure of some examples of the prepared compounds (Tables 1 and 2).

Copolymerization

In the present investigation, the copolymerization reactions and feed composition for M₁ with Mm₂, Mm₄, Mm₆, and/or Mm₈, are represented in Scheme 1 and Table 3. The prepared copolymers are soluble in most organic solvents, pale yellow viscous liquid and converted to pale yellow solid after sulfation and neutralization with sodium hydroxide.

Surface Properties

Surface and Interfacial Tensions

The measured values of surface and interfacial tensions of the prepared copolymeric surfactants are given in Table 4. The surface and interfacial tensions increased with increasing the hydrophobicity in copolymeric products. In the same time, increasing the percentage of oxypropenoxy sulfate moiety in the prepared copolymeric surfactants

TABLE 1

Microanalytical data of the prepared decylacrylate (M₁) and oxypropylated maleate ester, Mm₂, Mm₄, Mm₆, and Mm₈

Compound number	Mol. Form.	Mol. wt.	Yield%	Color State	Microanalysis			
					C%		H%	
					Calc.	Fd.	Calc.	Fd.
M ₁	C ₁₃ H ₂₄ O ₂	212.29	97	Colorless liquid	73.54	73.41	11.38	11.24
Mm ₂	C ₁₀ H ₁₆ O ₆	232.22	86	Pale yellow liquid	51.72	51.52	06.94	06.73
Mm ₄	C ₁₆ H ₂₈ O ₈	348.37	89	Pale yellow liquid	55.16	55.00	08.10	08.09
Mm ₆	C ₂₂ H ₄₀ O ₁₀	464.55	85	Pale yellow liquid	56.86	56.60	08.68	08.43
Mm ₈	C ₂₈ H ₅₂ O ₁₂	580.71	88	Pale yellow liquid	57.91	57.80	09.03	09.00

TABLE 2
Spectral data of some representing examples for decylacrylate, oxypropylated maleic acid, copolymeric anionic surfactants

Compound no.	¹ HNMR (δ = ppm)	IR (ν /cm ⁻¹)
M ₁	δ 0.85 (t, 3H, term.CH ₃); δ 1.0–1.5 (br s, 16H, CH ₂ chain); δ 4.0 (t, 2H, –COO–CH ₂ –CH ₂ –); δ 5.90(d, 1Ha, one proton Ha(Hb)C=CH–COOCH ₂ –). δ 5.95 (t, 1H, CH ₂ =CH–COOCH ₂ –) and δ 6.25(d, 1Hb, the 2nd proton of Ha(Hb)C=CH–COOCH ₂ –).	3120 (ν_{C-H} olefinic proton); 2980, 2930 (ν_{C-H} aliphatic), 1745 ($\nu_{C=O}$ of ester); 1630 ($\nu_{C=C}$) and 1450, 1260, 1150 (ν_{C-O}) respectively.
Mm ₂	δ 1.20 (d, 6H, term. CH ₃ in propylene oxide (PO)); δ 3.2(m, 2H, 2 (CH(CH ₃)–O) –H); δ 4.1 (d, 4H, (COOCH ₂) ₂); δ 5.3 (s, 2H, 2(–OH)) and δ 6.25 (d, 2H, –OOC–CH=CH–).	3460 (ν_{O-H}); 3130 (ν_{C-H} olefinic); 2950, 2930, 2860 (ν_{C-H} aliphatic); 1735, 1735 ($\nu_{C=O}$ of ester), 1620 ($\nu_{C=C}$ olefinic); 1460, 1240, 1160, 1100 (ν_{C-O-C} with high intensity in M _{n8} and decreasing gradually to lower intensity in M _{m2}).
PMm _{6e}	δ 0.80 (t, 3H, term.CH ₃ in fatty chain); δ 0.95–1.2 (br s, 16H, CH ₂ chain); δ 1.4 (d, 18H, term.CH ₃ in propylene oxide unit.); δ 3.1 (m, 6H, –{CH ₂ CH(CH ₃)–O} ₆ –H); δ 3.85 (d, 12H, 2 –(CH ₂ CH (CH ₃)–O) ₃ –H) δ 4.15 (t, 2H, –COO–CH ₂ –CH ₂ –), δ 5.3 (s, 2H, 2(–OH)) and with discharge of olefin protons.	
PMmS2e	δ 0.90 (t, 3H, term.CH ₃); δ 1.0–1.3 (br s, 16H, CH ₂ chain); δ 1.35 (d, 6H, term.CH ₃ in propylene oxide unit.); δ 3.1 (m, 2H, –(CH ₂ CH(CH ₃)–O) ₂); δ 3.75(d, 4H, O–CH ₂ –CH(CH ₃)–OSO ₃ [–] Na ⁺), δ 4.10 (t, 2H, –COOCH ₂ –CH ₂ –) and δ 5.29 (m, 2H, –CH ₂ –CH(CH ₃) ₂ –OSO ₃ [–] Na ⁺) with discharge of olefinic protons.	2980, 2950 (ν_{C-H} aliphatic); 1737 ($\nu_{C=O}$ of ester); 1450, 1240, 1100(ν_{C-O-C}) and 1180, 1090, 680 (characteristics for ν_{SO_2} , ν_{S-O} respectively).
PMmS4e	δ 0.90 (t, 3H, term.CH ₃); δ 1.0–1.3 (br s, 16H, CH ₂ chain); δ 1.40 (d, 12H, term.CH ₃ in propylene oxide unit.); δ 3.1 (m, 2H, –(CH ₂ CH(CH ₃)–O) ₂); δ 3.90 (d, 8H, O–CH ₂ –CH(CH ₃)–OSO ₃ [–] Na ⁺), δ 4.15 (t, 2H, –COO–CH ₂ –CH ₂ –) and δ 5.10 (m, 2H, –CH ₂ –CH(CH ₃) ₂ –OSO ₃ [–] Na ⁺) with discharge of olefinic protons.	
PMmS6g	δ 0.90 (t, 3H, term.CH ₃); δ 1.0–1.3 (br s, 16H, CH ₂ chain); δ 1.33 (d, 18H, term.CH ₃ in propylene oxide unit.); δ 3.2 (m, 2H, –(CH ₂ CH (CH ₃)–O) ₂); δ 3.80(d, 4H, O–CH ₂ –CH(CH ₃)–OSO ₃ [–] Na ⁺), δ 4.10 (t, 2H, –COO–CH ₂ –CH ₂ –) and δ 5.15 (m, 2H, –CH ₂ –CH(CH ₃) ₂ –OSO ₃ [–] Na ⁺) with discharge of olefinic protons.	

TABLE 3
Feed composition of anionic copolymeric surfactants PMm_{2a-i}

Compound number	MS1 : M1	Weight (gm)				Mole		Solvent ml	Yield %	Average Mol. wt. of polymer
		Initiator	a	W _{Mm2}	W _{M1}	M _{Mm2}	M _{M1}			
PMm _{2a}	0.1 : 0.9	0.0605	0.1111	0.6635	5.4589	0.0029	0.0259	5.00	82	37483
PMm _{2b}	0.2 : 0.8	0.0484	0.2500	1.3269	4.8523	0.0057	0.0228	4.00	79	73176
PMm _{2c}	0.3 : 0.7	0.0484	0.4285	1.9905	4.2460	0.0086	0.0200	4.00	85	76554
PMm _{2d}	0.4 : 0.6	0.0436	0.6669	2.6539	3.6394	0.0114	0.0171	3.60	76	33579
PMm _{2e}	0.5 : 0.5	0.0440	1.0100	3.3174	3.0328	0.0143	0.0143	3.62	83	67848
PMm _{2f}	0.6 : 0.4	0.0440	1.5138	3.9809	2.4263	0.0171	0.0114	3.62	76	43588
PMm _{2g}	0.7 : 0.3	0.0439	2.3518	4.6444	1.8197	0.0200	0.0086	3.63	79	39084
PMm _{2h}	0.8 : 0.2	0.0439	4.0277	5.3079	1.2130	0.0228	0.0057	3.62	76	36372
PMm _{2i}	0.9 : 0.1	0.0438	9.0888	5.9714	0.6065	0.0257	0.0028	3.62	74	87794

through each series leads to a decrease in the values of surface and interfacial tensions. This phenomenon is due to the increasing in hydrophilicity of the surfactant molecules that causes a decrease in the concentration of the surfactants at the surface.^[29,30]

Kraft Point

The recorded data in Table 4, showed that the copolymeric surfactants with higher percentage of hydrophilic monomers satisfy lower values of Kraft point (T_{KP}). This, might lead to a wide uses in industrial applications.^[30]

Wetting Time

The wetting properties of a surfactant is one of its most important surface properties. For example, in laundry cleaning or textile processing, the wetting of surfactants may accelerate the diffusion or penetration of alkali chemicals and dyes into fibers and improve the detergency or dyeing effects. From the measured data of the wetting time for the prepared copolymeric surfactants are illustrated in Table 4. Wetting time decreased with the decrease of hydrophilic unit in the copolymeric chain, while the effect of the hydrophobic moiety is negligible.^[30] In general, poor wetting times of copolymeric surfactants are recorded for PMmS2 with lower propylene oxide ratios (2 mole).

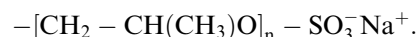
Foaming Height

Low-foaming tendency of surfactants is recently considered as an important property in some applications such as dyeing auxiliaries in modern textile dyeing industry. From the data recorded, copolymeric surfactants (PMmS₈)_{a-i} reveal higher foam than (PMmS₆, PMmS₄ and/or PMmS₂)_{a-i} (Table 4), respectively. The relative low-foaming properties of the copolymeric surfactants containing oxypropenoxy sulfate groups are probably due to the presence of multi-hydrophilic groups causing a considerable increase in the area per molecule and producing less

cohesive forces at the surface. Moreover, the repeating $-\text{SO}_3^- \text{Na}^+$ of oxypropylated groups, are believed to coil shape in the aqueous phase and decreasing the cohesive force due to intra-intermolecular hydrogen bond.^[30]

Stability to Hydrolysis

Copolymeric surfactants [PMmS₂, PMmS₄ PMmS₆ and PMmS₈]_{a-i} exhibited excellent stability in acidic medium more than basic media. This might be due to the easily hydrolysis of the ester groups cooperated with the propenoxy groups.^[30]



Emulsification Stability

It was reported that, better emulsifying properties were obtained with derivatives containing propylene oxide incorporated with $-\text{SO}_3^- \text{Na}^+$ into their structure.^[30] From the data given in Table 4, the prepared compounds exhibit an excellent degree to form emulsions either O/W or W/O for those with high percent of hydrophobicity.

Ca^{+2} Stability

Copolymeric surfactants with high percentage of propylene oxide (PMmS₈)_{a-i} revealed more tolerance towards very hard water (Table 4).

Dispersible Properties

The influence of the carrier (PMmS_{2e}, PMmS_{4e}, PMmS_{6e}, and/or PMmS_{8e}) on the diffusion rate of the dye decreases with increasing the molecular weight of the dye. Values of the absorption bands of the surfactants molecules increase with increasing the electron-donating groups in dye and the number of propylene oxide units for the tested copolymeric surfactants (Table 5). Purified dispersed dyes are hydrophobic and almost insoluble in

TABLE 4
Surface properties of anionic copolymeric surfactants PMmS_{(2,4,6 and 8)a-i}

Compound number	S.T. (dyne/cm) 0.1%	I.F.T. (dyne/cm) 0.1%	Kraft P.0.1%°C	Wet. t. 0.1% (sec.)	Foam h. 0.1% (mm.)	Emul. Stab. 20 mmole (sec)	Ca ²⁺ Stability (ppm)	Stability to hydrolysis (Base) (Acid) min. : sec. min. : sec.
PMmS _{2a}	59.5	18.0	32.0	—	—	190	1800	49 : 55 275 : 36
PMmS _{2b}	52.0	15.5	25.0	89.0	—	289	1850	50 : 46 286 : 29
PMmS _{2c}	36.5	15.0	09.0	69.0	190	597	2000	53 : 27 290 : 38
PMmS _{2d}	35.5	12.5	<0	49.0	210	598	2250	58 : 07 310 : 24
PMmS _{2e}	30.5	08.0	<0	37.0	255	621	2200	56 : 32 315 : 42
PMmS _{2f}	31.5	09.5	<0	26.0	260	643	2350	68 : 44 318 : 03
PMmS _{2g}	33.5	10.5	<0	29.0	270	685	2400	76 : 39 321 : 59
PMmS _{2h}	38.5	11.0	05.0	48.0	290	753	2450	81 : 33 369 : 06
PMmS _{2i}	49.5	16.0	03.0	53.0	310	780	2450	84 : 40 398 : 29
PMmS _{4a}	57.5	15.0	33.0	50.0	—	237	1900	52 : 55 277 : 36
PMmS _{4b}	51.0	13.5	23.0	86.0	—	244	2000	61 : 48 290 : 29
PMmS _{4c}	34.5	12.0	08.0	75.0	230	495	2100	63 : 21 305 : 31
PMmS _{4d}	33.5	10.0	<0	59.0	270	490	2400	68 : 47 314 : 44
PMmS _{4e}	30.0	07.5	<0	46.0	285	521	2400	69 : 05 319 : 49
PMmS _{4f}	30.5	08.0	<0	37.0	290	531	2400	78 : 37 332 : 13
PMmS _{4g}	32.0	09.5	<0	34.0	300	570	2400	86 : 00 339 : 49
PMmS _{4h}	37.0	09.0	04.0	20.0	305	655	2500	88 : 23 381 : 26
PMmS _{4i}	47.0	14.0	06.0	32.0	320	689	2600	89 : 33 402 : 44
PMmS _{6a}	56.0	14.5	29.0	49.0	—	307	1950	57 : 12 283 : 21
PMmS _{6b}	50.5	13.0	14.0	83.0	120	321	2100	59 : 27 289 : 00
PMmS _{6c}	33.0	11.0	04.0	78.0	190	590	2150	64 : 38 291 : 12
PMmS _{6d}	32.5	09.0	00.0	62.0	240	592	2200	68 : 17 297 : 53
PMmS _{6e}	29.5	07.0	00.0	55.0	260	621	2400	76 : 28 305 : 12
PMmS _{6f}	30.0	07.5	00.0	43.0	270	631	2400	79 : 03 312 : 05
PMmS _{6g}	31.0	09.0	00.0	40.0	290	650	2450	89 : 31 321 : 00
PMmS _{6h}	36.0	08.0	02.0	23.0	310	664	2500	91 : 05 332 : 51
PMmS _{6i}	45.5	13.5	03.0	30.0	330	670	2600	93 : 50 368 : 42
PMmS _{8a}	50.0	13.5	14.0	38.0	—	342	2000	61 : 22 291 : 11
PMmS _{8b}	48.5	12.0	08.0	42.0	200	370	2100	69 : 08 301 : 05
PMmS _{8c}	31.5	11.0	01.0	60.0	250	480	2150	71 : 12 313 : 12
PMmS _{8d}	28.5	09.0	00.0	53.0	280	542	2200	78 : 52 327 : 03
PMmS _{8e}	29.0	08.0	00.0	51.0	290	567	2400	81 : 00 336 : 19
PMmS _{8f}	31.0	06.0	00.0	47.0	295	592	2500	92 : 15 340 : 00
PMmS _{8g}	31.5	07.0	00.0	31.0	320	598	2550	93 : 20 353 : 12
PMmS _{8h}	38.5	08.0	00.0	18.0	330	605	2620	96 : 03 369 : 32
PMmS _{8i}	45.5	12.0	00.0	22.0	340	612	2630	99 : 13 378 : 10

TABLE 5
Characterization spectra of the dispersed dye with the water-soluble anionic co-polymeric surfactants PMmS_{2d}, PMmS_{4d}, PMmS_{6d}, and PMmS_{8e} at 25°C

Dispersant dye			PMmS _{2d} λ		PMmS _{4d} λ		PMmS _{6d} λ		PMmS _{8e} λ	
			(nm)	d*	(nm)	d*	(nm)	d*	(nm)	d*
Rhodanine azo-dye	X									
	–H	A ₁	405	1.10	410	1.14	415	1.18	422	1.20
	–CH ₃	A ₂	445	1.41	450	1.45	455	1.48	455	1.51
	–OCH ₃	A ₃	340	1.72	346	1.76	350	1.79	359	1.83
Antipyrine azo-dye	X									
	–H	B ₁	375	1.20	381	1.23	383	1.25	386	1.29
	–CH ₃	B ₂	360	1.44	365	1.47	370	1.49	370	1.52
	–OCH ₃	B ₃	395	0.85	415	0.89	425	0.92	430	0.98
	–NO ₂	B ₄	425	1.80	435	1.84	440	1.89	442	1.94

d*: Optical density.

water. Surfactant carrier increases the solubility of dyes, which can be explained as the separation of charge due to the resonance on the molecules under the influence of the substituent groups. On the other hand, low aqueous solubility is attributed to hydrophobic bonding causing aggregation and precipitation when the concentration increases more than 1 gm/100 ml. The most important considerations for the development of the RPP-Supra process are the selection of disperse and reactive dyes,^[31–33] as well as the determination of the optimum pH 7.5 to achieve the maximum yield of the reactive dyes with the decreasing of temperature.^[34–36] The molecular weight of the used insoluble dyes Rhodanine azo-dyes is higher than that of

Antipyrine azo-dyes. The order of the dispersability percent of some selected copolymeric surfactants (Table 6, and Figure 1) is as follows:

$$\text{PMmS}_{2e} < \text{PMmS}_{4e} < \text{PMmS}_{6e} < \text{PMmS}_{8e}$$

Biodegradability

After use, all surfactants used in laundry detergents, cleaning agents, and dyeing auxiliaries are passed quantitatively into wastewater. Because of this fact, the constant input of surfactants into the environment requires a particular ecological characterization of this class of compounds. An excellent review of surfactant biodegradability

TABLE 6
Dispersability percentage of water-soluble anionic co-polymeric surfactants PMmS_{2d}, PMmS_{4d}, PMmS_{6d}, and PMmS_{8e}

Dispersant dye			PMmS _{2d}	PMmS _{4d}	PMmS _{6d}	PMmS _{8e}
			D %			
Rhodanine azo-dye	X					
	–H	A ₁	46.0	50.30	53.60	56.36
	–CH ₃	A ₂	48.10	56.70	59.10	63.60
	–OCH ₃	A ₃	55.20	60.22	68.82	73.00*
Antipyrine azo-dye	X					
	–H	B ₁	51.30	53.60	55.70	60.30
	–CH ₃	B ₂	54.60	57.80	61.00	63.00
	–OCH ₃	B ₃	62.30	69.50	70.00	73.40*
	–NO ₂	B ₄	48.00	51.80	57.00	59.00

*Highest dispersability %.

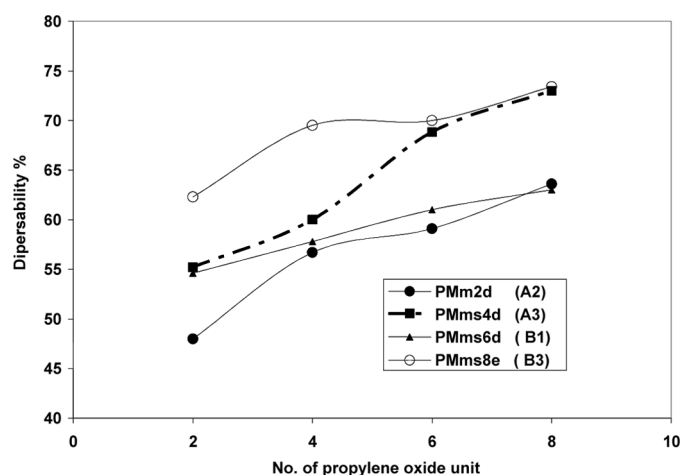


FIG. 1. Dispersability percent of the insoluble dye A2, A2, B1, and B3 by water-soluble anionic copolymeric surfactants (PMms2d, PMms4d, PMms6d, and PMms8e).

points out that biodegradability increases with increasing linearity of the hydrophobic group and is reduced, for isomeric materials, by branching in that group.^[37,38] On other hand, the presence of hydrophilic groups mainly affects the degradation rate of the surfactants, but not their ultimate. Biodegradability is deterred and degradation is slowed as steric hindrance increases.^[39,40] The results of biodegradability of [PMmS₂, PMmS₄, PMmS₆, and/or PMmS₈]_{a-i} (Figure 2), reflect the fact that: it decreases with increasing the number of repeating units of propenoxy groups as well as, the repeating alkyl groups in hydrophobic unit.^[30] Moreover, PMmS_{2a-i} recorded higher degree of degradation than other prepared copolymeric surfactants.

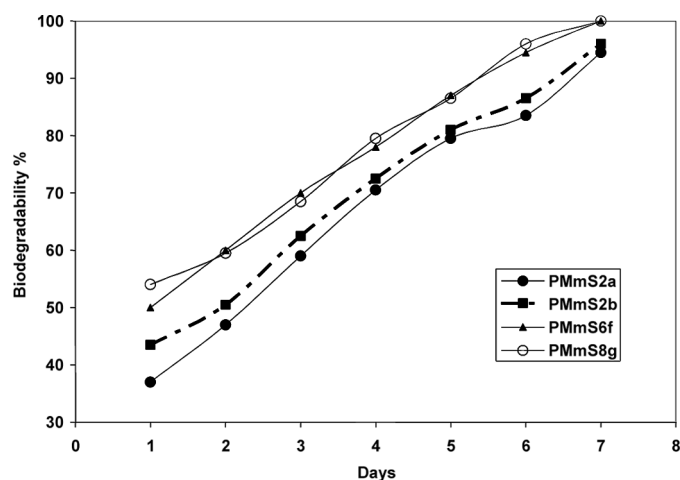


FIG. 2. Biodegradability percent of water-soluble anionic copolymeric surfactants (PMms2a, PMms2b, PMms6f, and PMms8g).

CONCLUSION

These surfactants exhibit good surface activities, including surface tension, moderate foaming, and wetting power. These surfactants have excellent properties, in that they are much more biodegradable than traditional surfactants. The excellent dispersability for the used commercial dye, was recorded with copolymeric surfactants of higher percentage of propylene oxide with molar ratio 8 moles incorporated with $-\text{SO}_3^- \text{Na}^+$ (PMmS_{8d}). Further studies regarding will be performed for utilization of fatty derivatives of industrial vegetable seeds to preparing of such most important compounds.

REFERENCES

- [1] Hsu, K.C., Lee, Y.F., and Chian, S.Y. (1995) *J. Appl. Polym. Sci.*, 57: 1205.
- [2] Lin, S.Y. (1981) *Text Chem. Colorist*, 13: 261.
- [3] Cochran, D. and Laschewsky, A. (1997) *Macromolecules*, 30: 2278.
- [4] Attwood, D. and Florence, A.T. (1983) *Surfactant Systems*; London: Chapman and Hall; pp. 469.
- [5] Boyd, J., Parkinson, C., and Sherman, P. (1972) *J. Colloid Interface Sci.*, 41: 359.
- [6] Zaki, N.N., Abdel-Raouf, M.E., and Abdel-Azim, A.A.A. (1996) *Monashefte Für Cemie*, 127: 621.
- [7] Schmolka, I.R. (1977) *J. Am. Oil Chem. Soc.*, 54: 110.
- [8] Azab, M.M., Bader, S.K., and Shaaban, A.F. (2001) Preparation and evaluation of some water-soluble polyester surfactants. *J. Appl. Polym. Sci.*, 81: 3413.
- [9] Poutov, V.D., Anufrieva, E.V., and Krakovyo, M.G. (1998) *Chim J. Polym. Sci.*, 16: 268.
- [10] Schuter, J. (1957) *Text. Res.*, 27: 352.
- [11] Weisz, I. (1967) *Trans. Faraday Soc.*, 63: 1801.
- [12] El-DougDoug, W.I.A. and Ahmed, M.H.M. (2004) *J. Oil Soap Cosmetics*, 53 (2): 63.
- [13] El-DougDoug, W.I.A. and Mahmoud, A.A. (2002) *J. Pigment Resin Technol.*, 31 (3): 148.
- [14] El-DougDoug, W.I.A. and Azab, M.M. (2001) *J. Pigment Resin Technol.*, 30 (6): 380.
- [15] Casotti, H. (1974) *Tenside Deterg.*, 11: 202.
- [16] El-Sawy, A.A., El-Dib, F., and Fadel, H.M. (1989) *J. Koloriztsikai Ertesito*, 3-4: 42.
- [17] Schildnecht, C.E. (1952) *Vinyl and Related Polymers*; New York: Wiley.
- [18] Azab, M.M. (2005) *Polym. Int.l.*, 54: 161.
- [19] Findly, A. (1963) *Practical Physical Chemistry*; 6th ed.; London: Longmans, London; p. 1040.
- [20] Weil, J.K., Smith, F.D., Stirton, A.J., and Bistlin, R.G. Jr. (1963) *J. Am. Oil Chem. Soc.*, 40: 538.
- [21] Draves, C.Z. and Clarkes, R. (1931) *J. Am. Dye Stuff Reporter*, 20: 201.
- [22] Ross, J. and Miles, G.D. (1941) *Oil and Soap*, 18: 99.
- [23] Takeshi, H. (1970) *Bull. Chem. Soc. LB*, 2236. (Japan).
- [24] El-Sukkary, M.M.A., El-Sawy, A.A., and El-Dib, F. (1987) *Hungarian J. Industr. Chem.*, 15: 417.
- [25] Wilkes, B.G. and Wiekert, J.N. (1973) *Ind. Eng. Chem.*, 22: 1234.

- [26] Abe, N. (1979) *Dyeing Ind.*, 54: 110.
- [27] Chen, K.M. and Liu, H.J. (1987) *J. Appl. Polym. Sci.*, 34: 1879.
- [28] Eter, E.T., Richard, R.E., and Darid, A. (1974) *J. Am. Oil Chem. Soc.*, 51: 486–494.
- [29] Elworthy, P.H. and Macfarlane, C.B. (1962) *J. Pharm. Pharmacol.*, 14: 100.
- [30] Falbe, J. (1986) In *Surfactants for Consumer*, Heidelberg: Springer-Verlager, chap. 4.
- [31] Dickly, J.B. and Towne, E.B. (1953) U.S. Patent 2.659.719.
- [32] Towne, E.B., Dickly, J.B., and Bloom, M.S. (1958) U.S. Patent 2.839.523.
- [33] Senryo, G., Kentu, G., and Koho, K.T. (1983) JP 59,215,355.
- [34] Azab, M.M., Bader, S.K., and Shaaban, A.F. (2002) *Pigm. Resin Technol.*, 31: 138.
- [35] El-DougDoug, W.I.A. and El-Mossalamy, E.H. (2006) *J. Applied Surface Sci.*, 253: 2487.
- [36] Fisichella, S. (1981) *J. Text. Res.*, 5: 683.
- [37] Swisher, R.D. (1987) *Surfactant Biodegradability*; 2nd ed.; New York: Marcel Dekker; pp. 130–142.
- [38] Szymanski, A., Wyras, B., Zbigniew, S., Jaroszynski, T., and Lukaszewski, Z. (2000) *Water Res.*, 34: 410.
- [39] Chen, L., Hu, Z., and Zhu, H. (2008) *J. Surfact. Deterg.*, 11: 97–102.
- [40] Yasin, S.A. and El-DougDoug, W.I. A. (2010) *J. Dispersion Sci. Technol.*, 31: 1033–1042.