Preparation and Evaluation of Some Water-Soluble Polyester Surfactants

M. M. AZAB, S. K. BADER, A. F. SHAABAN

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

ABSTRACT: A novel series of water-soluble polyester surfactants were prepared by the polymerization of bis-1,4-(dicarboxymethoxy) benzene, maleic anhydride, and oxypropylated 1,4-butane diol (IP_1–IP_5) or oxypropylated 1,6-hexane diol (IIP_1–IIP_5). The unique structural features of these surfactants were confirmed by IR and ^{1}H-NMR spectra. These water-soluble polyester surfactants exhibited excellent surface tension, interfacial tension, low foaming, good emulsifier capability, and good biodegradability in river water, solubilization, wetting, and dispersant properties for applied dyes. The antimicrobial and antifungal properties of the prepared polyester surfactants were measured and found to be highly active. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3413–3424, 2001

Key words: water-soluble polyester surfactants; surface tension; interfacial tension; foaming; emulsifier; wetting; biodegradability solubilization; dispersant; antimicrobial; antifungal

INTRODUCTION

A *surfactant* is a substance that has a characteristic molecular structure consisting of a hydrophobic portion together and a polar or ionic portion. When a surfactant is present in a low concentration in a system, it has the property of adsorbing onto the surfaces or interfaces of the system and of altering, to a marked degree, the surface or interfacial properties.

Many water-soluble polymers are used as surfactants because of their amphipathic structure and surface activities similar to those of traditional surfactants. For example, lignosulfonates exhibit excellent dispersant properties in a disperse or vat dye system,[1–3] polysorbates exhibit excellent emulsifying properties for an oil-in-water system,[4,5] and polyoxyethylene–polyoxypropylene–polyethylene block copolymers, known by their generic name as *poloxamers*, exhibit properties such as deemulsification, dispersion, and emulsion stabilization.[6,7]

Water-soluble polyesters prepared from dicarboxylic acid and diol have been used mainly in the paint industry. However, only limited information is available in regard to water-soluble polyesters as surfactants in polymers that have an amphipathic molecular structure similar to the structures of traditional surfactants.[8]

This article describes the preparation and surface active properties of a novel series of water-soluble polyester surfactants.

EXPERIMENTAL

Materials

Maleic anhydride, phthalic anhydride, itaconic acid, hydroquinone, monochloroacetic acid, so-

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dium hydroxide, sodium hydrogen bisulfite, n-octanol, citric acid, and sodium carbonate were Merck (Darmstadt) products. Benzoyl peroxide, 1,6-hexane diol, and 1,4-butane diol were obtained from Aldrich (Steinheim, Germany).

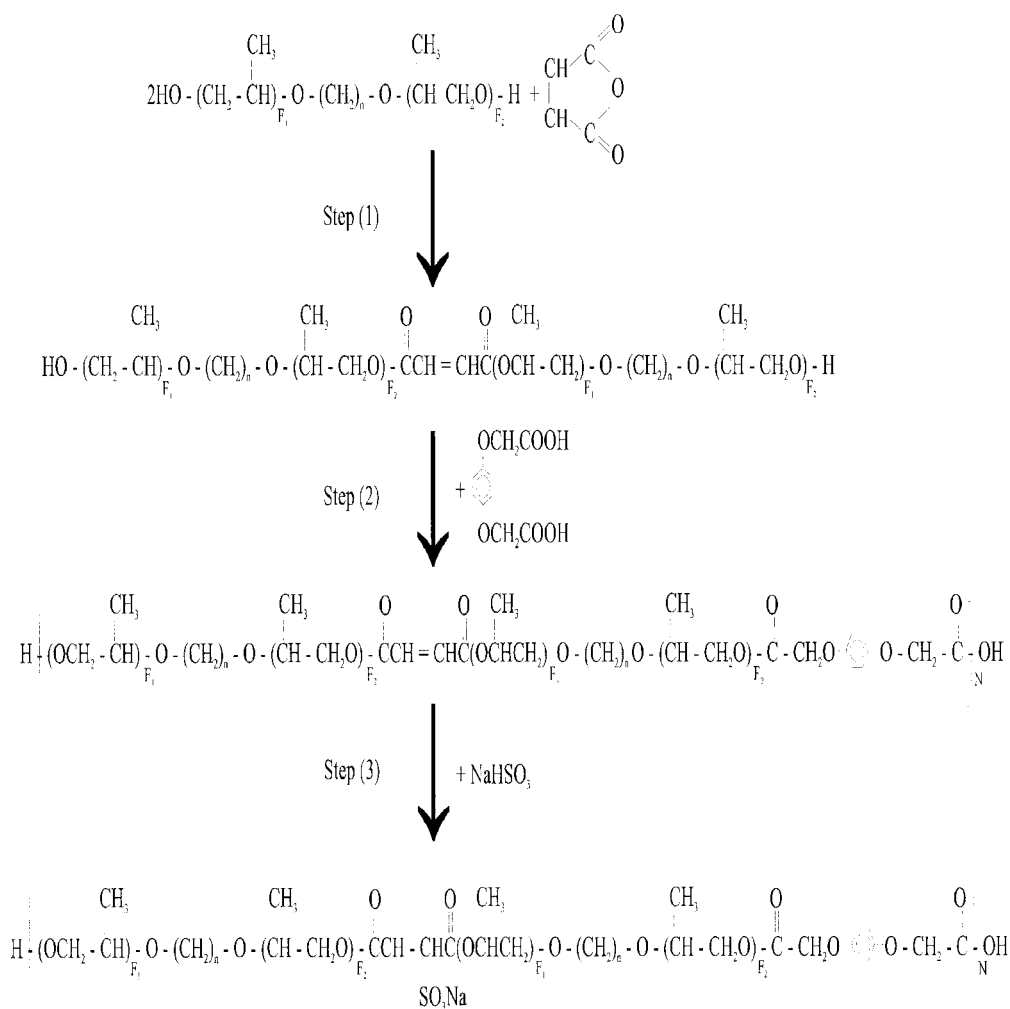### Methods

Preparation of Bis-1,4-(dicarboxymethoxy) Benzene

Bis-1,4-(dicarboxymethoxy) benzene was prepared according to a previous method.[9]

Preparation of Water-Soluble Polyester Surfactants

The water-soluble polyester surfactants were prepared in three steps: the first step involved the reaction of maleic anhydride with oxypropylated diol at 180–200°C, the second step reacted the products obtained in the first step with bis-1,4-(dicarboxymethxy) benzene at 240–250°C, and the third step introduced the sulfonate group by the reaction of the products from the second step with sodium hydrogen bisulfite at 120°C. Because the reactions of the first two steps were revers-

Results and Discussion

The following scheme describes the preparation of the novel series

of water-soluble polyester surfactants:

Scheme 1 Preparation of the novel series of water-soluble polyester surfactants where $n = 4$ and 6; $F_1 + F_2 = 5$, 10, 15, 20, and 25; and N is the degree of polymerization.

ible, the water had to be continuously removed from the system to maintain the reaction in a forward direction. The following example shows a typical recipe for preparing a water-soluble polyester that involved maleic anhydride, bis-1,4-(dicarboxymethoxy) benzene, and oxypropylated 1,4-butane diol [molecular weight (MW) = 380].

A reaction mixture containing 57 g (0.5 mol) of maleic anhydride and 380 g (1 mol) of oxypropylated 1,4-butane diol was stirred mechanically and heated to 180–200°C under a nitrogen atmosphere. The temperature was held there until 9 mL (0.5 mol) of water was trapped. Next, 113 g (0.5 mol) of bis-1,4-(dicarboxymethoxy) benzene was added, and the mixture was reheated to 240–250°C. The reaction was followed until another 9 mL (0.5 mol) of water was trapped (3 h). Then, the product was cooled to 120°C, and 62 g (0. 5 mol) of sodium bisulfite was added. After stirring for 2 h at the same temperature, the product was cooled.

Analysis

The acid and hydroxyl values were determined by the usual methods described elsewhere, and from these values, the MWs of the water-soluble polyesters were calculated.[6] The sulfonante-group (SO_3Na) content was determined by the method described in JLS K 3366.

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

Measurements

Surface tension was determined at room temperature with a Du-Nouy international tensiometer,[10] (Fisher, Germany).

Foaming properties were determined by the Ross–Mile method with a foam accumulate measuring system, whereas the foaming production was measured by the height of the foam initially produced. The foaming stability was measured by the height after 3 min.[11]

Solubilization was measured by a common method, in which a 50-mL solution was shaken with 40 mg of purified dispersed dye and various concentrations of water-soluble polyesters for 48 h at 30°C. The insoluble dyes were filtered off through a glass filter, solubilized dyes were extracted from the filtrate by toluene, and their concentrations were determined spectrophotometrically.[12]

Dispersing properties were determined by the following method: A 100-mL solution of 0.1 g of commercial dispersed dye 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 1 h. After this treatment, the solution was 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 dispersibility was calculated as follows:[13]

Table I   Analytical Data and Physical Properties of Water-Soluble Polyester Surfactants Based on Oxypropylated 1,4-Butane Diol (IP$_1$–IP$_5$) and 1,6-Hexane Diol (IIP$_1$–IIP$_5$)

Polyester	$(F_1 + F_2)^a$	Nature of Polyester	Acid Value	OH Value	MW of Polyester	N^b
IP$_1$	5	Yellowish resin	21.18	22.13	13,608	12
IP$_2$	10	Yellowish resin	18.75	19.23	22,282	13
IP$_3$	15	Yellowish resin	22.14	25.12	25,234	11
IP$_4$	20	Yellowish resin	18.31	20.17	40,236	14
IP$_5$	25	Yellowish resin	25.82	27.18	34,540	10
IIP$_1$	5	Yellowish resin	20.95	24.08	14,280	12
IIP$_2$	10	Yellowish resin	18.36	21.42	24,780	14
IIP$_3$	15	Yellowish resin	16.50	18.07	35,250	15
IIP$_4$	20	Yellowish resin	19.55	22.35	32,230	11
IIP$_5$	25	Yellowish resin	21.73	24.17	42,120	12

[a] Total number of repeating units of propylene glycol in the oxypropylated 1,4-butane diol and 1,6-hexane diol.
[b] Degree of polymerization.

Table II ^{1}H-NMR Spectral Data of Water-Soluble Polyester Surfactants Based on Oxypropylated 1,4-Butane Diol (IP$_1$–IP$_5$) and 1,6-Hexane Diol (IIP$_1$–IIP$_5$)

Polyester	Component	Chemical Shift δ (ppm)	Assignment	Number of Protons	Peak Areas (Integration)	Relative Mole Amount	Mole %
IP$_1$	Glycol	0.9–1.6, 2.9, and 3.9	10(CH$_3$),4-(CH$_2$O), 10(CH$_2$O), and 10(CHO)	76	55	0.723	49.863
	Acid	3.4, 4.8, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, with C=O, O, SO$_3$H	11	8	0.727	50.137
IP$_2$	Glycol	0.9–1.6, 3.4, and 3.8	20(CH$_3$), 4-(CH$_2$O) 20(CH$_2$O), and 10(CHO)	136	87	0.639	46.778
	Acid	3.4, 4.8, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, with C=O, O, SO$_3$H	11	8	0.727	53.222
IP$_3$	Glycol	1–1.5, 2.9–3.5, and 3.9	30(CH$_3$), 4-(CH$_2$O) 30(CH$_2$O), and 30(CHO)	196	91.5	0.46	43.81
	Acid	3.5, 4.7, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, with C=O, O, SO$_3$H	11	6.5	0.59	56.19
IP$_4$	Glycol	1.1–1.8, 2.2, 3.5, and 4	40(CH$_3$), 4-(CH$_2$O), 10(CH$_2$O), and 40(CHO)	156	190	0.72	49.32
	Acid	3.5, 4.7, and 7.0	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, with C=O, O, SO$_3$H	11	8	0.74	50.68
IP$_5$	Glycol	1–1.5, 4.8, and 3.9	50(CH$_3$), 4-(CH$_2$O) 10(CH$_2$O), and 50(CHO)	316	79.5	0.25	52.41
	Acid	3.5, 4.8, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, with C=O, O, SO$_3$H	11	2.5	0.227	47.59

|							
IIP$_1$	Glycol	1–1.4, 3.4, and 4.4	10(CH$_3$), 4-(CH$_2$), 4(CH$_2$O), 10(CH$_2$O), and 10(CHO)	84	84	1.0	50.00
	Acid	3.4, 4.7, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, SO$_3$Na	11	11	1.0	50.00
IIP$_2$	Glycol	1–1.4, 2.9–3.5, and 4.2	20(CH$_3$), 4-(CH$_2$), 4(CH$_2$O) 20(CH$_2$O), and 20(CHO)	144	81.5	0.56	52.83
	Acid	3.5, 4.7, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, SO$_3$Na	11	5.5	0.5	47.17
IIP$_3$	Glycol	1–1.4, 2.9–3.6, and 4.1	30(CH$_3$), 4-(CH$_2$), 4(CH$_2$O), 30(CH$_2$O), and 30(CHO)	205	88.5	043	44.11
	Acid	3.6, 4.7, and 6.9	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, SO$_3$H	11	6	0.54	55.89
IIP$_4$	Glycol	1–1.5, 3–3.6, and 4.1	40(CH$_3$), 4-(CH$_2$), 4(CH$_2$O) 40(CH$_2$O), and 40(CHO)	264	93.5	0.35	49.51
	Acid	3.6, 4.8, and 7.2	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, SO$_3$Na	11	4	0.36	50.49
IIP$_5$	Glycol	1–1.5, 3.4, and 3.8	50(CH$_3$), 4-(CH$_2$O), 4(CH$_2$O) 50(CH$_2$O), and 50(CHO)	324	110	0.339	48.497
	Acid	3.4, 4.7, and 7.0	2(OCH$_2$C) and (C—CH$_2$—CH—C) + 4Ar, SO$_3$Na	11	4	0.36	51.503
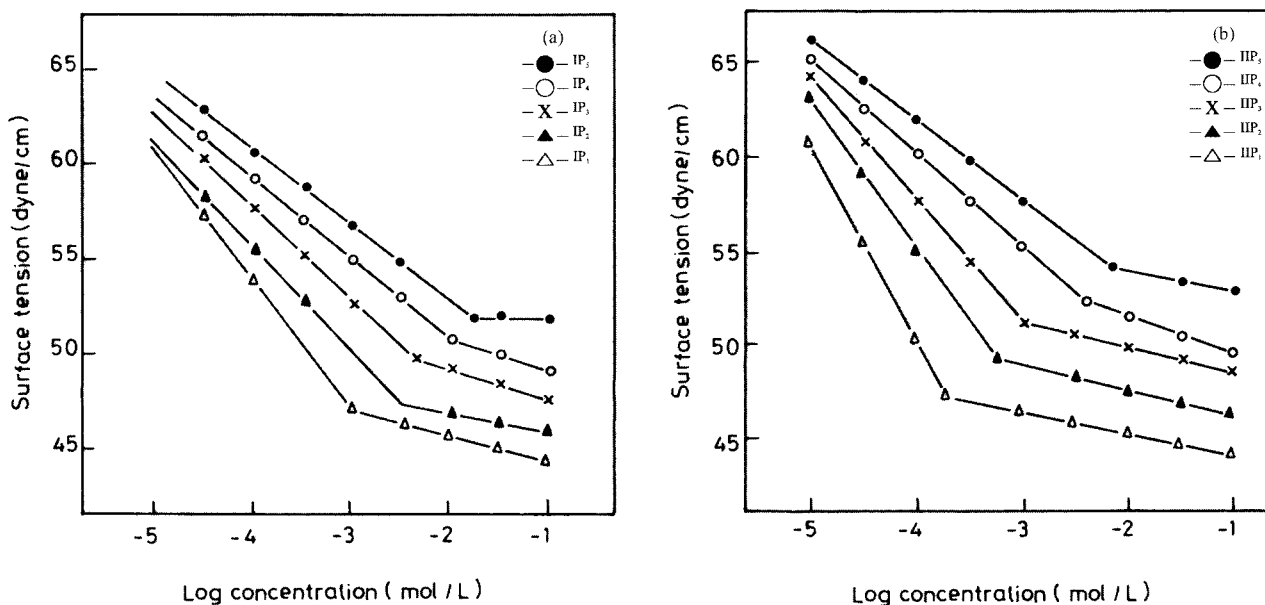
Figure 1 Plots of surface tension versus log molar concentration for water-soluble polyester surfactants at 25°C: (a) polyesters IP_1–IP_5 and (b) polyesters IIP_1–IIP_5.

Dispersibility (%)

$$= \frac{\text{Dye Concentration of Filtrate}}{\text{Dye Concentration of Original Solution}} \times 100$$

RESULTS AND DISCUSSION

Scheme 1 describes the preparation of the novel series of water-soluble polyester surfactants. The analytical data and physical properties of the water-soluble polyester surfactants are shown in Table I. All the tested polyesters were water-soluble polymers, and all were yellowish resins. The MWs of the polyesters ranged between 13,608 and 42,120.

The IR spectra of the water-soluble polyester surfactants showed a broad band at 3500 cm^{-1} caused by the γ OH of intermolecular hydrogen bonding, a strong band at 3050 cm^{-1} caused by the γ CH of aromatic residual, a band at 1720 cm^{-1} characteristic of the γ C—O ester group, and a strong band at 1100 cm^{-1} characteristic of the γ C—O bond.

The ^{1}H-NMR spectra of the water-soluble polyester surfactants gave further support to the assigned structure. The method of Baddar et al.[14] was used in this work for the qualitative and quantitative analyses of the copolymers by

^{1}H-NMR spectroscopy. The results of both qualitative and quantitative analyses of the copolyester resins are shown in Table II. Table II shows that the molar ratios of glycol to acid calculated for the copolyester surfactants were almost 50:50.

Surface Properties

The water-soluble polyesters prepared in this study were evidently of an amphipathic structure similar to the structures of traditional surfactants. The aromatic and saturated aliphatic residues were the hydrophobic portion; the sulfonate group (anionic) and polyoxypropylene chain (nonionic) were the hydrophilic portion. The surface activities of these water-soluble polyester surfactants are shown in Figure 1. The surface tensions of the solutions were reduced by the addition of the surfactants because of the amphipathic structure, which caused the concentration of the surfactant molecules at the surface and the reduction of surface tension.[15–17]

An increase in the length of polyoxypropylene chains of the nonionic portion resulted in a clear decrease in surface activity. This phenomenon was caused by the increase of the hydrophilic effect of surfactants, which helped the concentration of the surfactants at the surface decrease.[18]

Inflection points were observed in the curves. The concentration at the inflection point corre-

Table III   Surface Properties of Water-Soluble Polyester Surfactants Based on Oxypropylated 1,4-Butane Diol (IP_1–IP_5) and 1,6-Hexane Diol (IIP_1–IIP_5)

Polyester	$F_1 + F_2$	Surface Tension (dynes/cm) at 25°C	Interfacial Tension (dynes/cm) at 25°C	Kraft Point (°C)	(mol/L)	ν_{CMC} (dynes/cm)	Wetting Time (s)	Stability to Hydrolysis (min : s)		HLB
								H^+	OH^-	
IP_1	5	44.0	10.0	3	0.0010	47.0	47.0	Staple more than 24 h	11:10	10.229
IP_2	10	46.0	11.0	0	0.0015	47.5	47.5	Staple more than 24 h	03:55	08.226
IP_3	15	47.5	12.5	2	0.0017	50.0	50.0	Staple more than 24 h	04:42	10.235
IP_4	20	49.5	13.0	5	0.0100	51.0	51.0	Staple more than 24 h	06:25	11.658
IP_5	25	52.0	14.0	7	0.0130	52.0	52.5	Staple more than 24 h	06:43	11.842
IIP_1	5	45.0	10.5	0	0.0014	47.5	47.5	Staple more than 24 h	04:23	09.747
IIP_2	10	47.0	12.5	3	0.0016	49.5	49.5	Staple more than 24 h	04:56	13.107
IIP_3	15	49.0	13.0	0	0.0010	51.5	51.5	Staple more than 24 h	06:40	14.808
IIP_4	20	50.0	13.5	5	0.0016	52.0	52.0	Staple more than 24 h	09:17	15.836
IIP_5	25	53.0	15.0	9	0.0018	45.0	54.0	Staple more than 24 h	16:42	16.524

* Surface tension at critical micelle concentration.

sponds to the critical micelle concentration (cmc) in the cases of traditional surfactants.[19] The values found were smaller than the values of traditional surfactants because of the high MWs and large hydrophobic chains of the water-soluble polyester surfactants. The values increased according to the increase in the length of polyoxypropylene chains of the nonionic portion of the surfactants (more hydrophilic). The increase in the length of the saturated aliphatic chain from

Table IV   Foaming Properties of Water-Soluble Polyester Surfactants Based on 1,4-Butane Diol (IP$_1$–IP$_5$) and 1,6-Hexane Diol (IIP$_1$–IIP$_5$)

| Polyester | $F_1 + F_2$ | Foam Height (mm) | | | |
| | | 30°C | | 85°C | |
		Initial	3 min	Initial	3 min
IP$_1$	5	55	0	60	0
IP$_2$	10	60	0	60	0
IP$_3$	15	75	0	80	0
IP$_4$	20	95	0	90	0
IP$_5$	25	115	0	95	0
IIP$_1$	5	90	0	95	0
IIP$_2$	10	110	0	115	0
IIP$_3$	15	125	0	120	0
IIP$_4$	20	135	0	140	0
IIP$_5$	25	150	0	140	0

$(CH_2)_4$ to $(CH_2)_6$, as shown in Table III, led to a slight decrease in surface activity.

Wetting Properties

The prepared water-soluble polyester surfactants exhibited good wetting properties, as shown in Table III. An increase in the number of repeating units of polypropylene glycol led to a slight increase in wetting time. Also, a change in saturated aliphatic chain length from $(CH_2)_4$ to $(CH_2)_6$ led to a slight decrease of wetting time.[20]

Stability to Hydrolysis

All the prepared water-soluble polyester surfactants exhibited good stability, especially in acidic media, but slightly lower stability in the basic medium. The presence of the sulfonate group probably protected the ester linkage through steric hindrance. The change of the saturated aliphatic chain length from $(CH_2)_4$ to $(CH_2)_6$, as shown in Table III, led to a slight increase in stability in both acidic and basic media.[21]

Most of the prepared water-soluble polyester surfactants, as shown in Table III, exhibited good calcium stability. From this table, it is clear that hydrophile–lipophile balance (HLB) values of the prepared water-soluble polyesters ranged from 10 to 16.5.

Foaming Properties

The low-foaming tendency of surfactants is important in some applications such as dyeing aux-

Table V   Emulsifying Properties of Water-Soluble Polyester Surfactants Based on 1,4-Butane Diol (IP$_1$–IP$_5$) and 1,6-Hexane Diol (IIP$_1$–IIP$_5$)

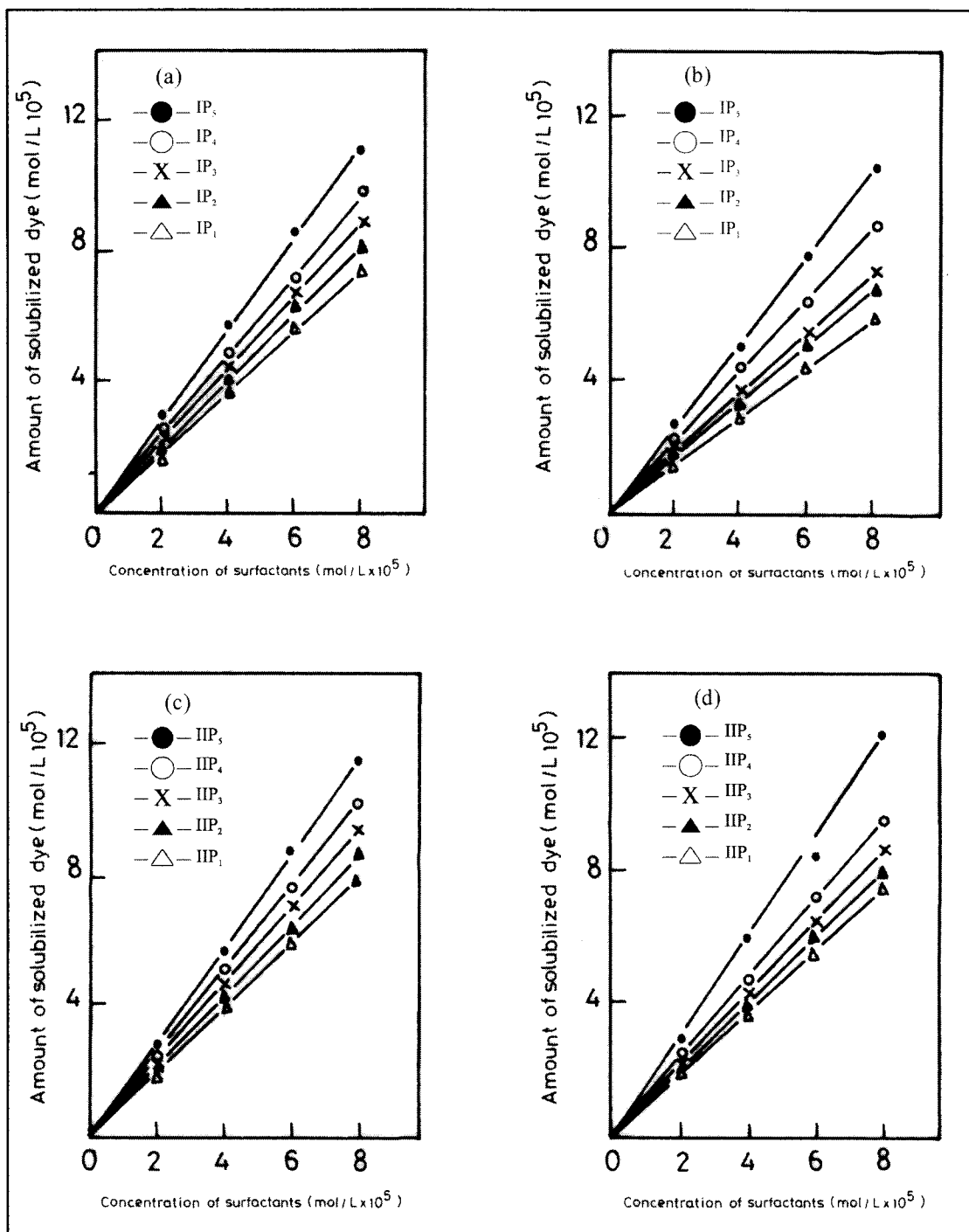| Polyester | $F_1 + F_2$ | Separation Time (min : s) | | |
		Liquid Parafin	Kerosene	o-Dichloro Benzene
IP$_1$	5	19:30	23:12	17:15
IP$_2$	10	17:45	18:30	15:22
IP$_3$	15	13:52	17:42	11:37
IP$_4$	20	12:40	09:15	13:33
IP$_5$	25	08:05	15:50	10:51
IIP$_1$	5	27:16	33:05	27:19
IIP$_2$	10	18:35	27:43	16:35
IIP$_3$	15	16:20	12:15	13:42
IIP$_4$	20	13:45	18:56	10:36
IIP$_5$	25	09:15	11:35	16:42

Figure 2 Plots of the amount of solubilized dye as a function of the surfactant concentration: (a) polyesters IP_1–IP_5 and dye 1; (b) polyesters IP_1–IP_5 and dye 2; (c) polyesters IIP_1–IIP_5 and dye 1; and (d) polyesters IIP_1–IIP_5 and dye 2.

iliaries in the modern textile-dyeing industry. The relative low-foaming properties of water-soluble polyester surfactants are shown in Table IV. All of these polyester surfactants provided not only low-foaming properties as measured by the height of the foam initially produced but also low-foaming stability. These low-foaming effects were probably caused by (1) the presence of mul-

tihydrophilic groups, which caused a considerable increase in the area per molecule and produced less cohesive forces at the surface; (2) the multianionic hydrophilic SO_3Na, which increased the electrostatic repulsion among surfactant molecules counteracting the interchain cohesive forces; and (3) the water-soluble polyesters that are believed to coil in the aqueous phase, which decreased the cohesive forces caused by intramolecular and intermolecular bonds. The foam height clearly increased by increasing the number of propylene oxide groups per molecule.[22]

Emulsifying Power

Emulsification is of immense importance to the technological development of surfactants. More recently, developed types are surface active agents in which the hydrophilic portion of the molecule comprises a multiplicity of ether oxygen of the hydroxyl groups. The emulsifying ability of water-soluble, polyester surfactants is shown in Table V, which indicates that all polyester surfactants exhibit good emulsifying power toward liquid paraffin, kerosene, and o-dichlorobenzene, as was expected. The change in saturated aliphatic chain length from $(CH_2)_4$ to $(CH_2)_6$ led to an increase in the separation time between the oil and aqueous phases, whereas an increase in the number of repeating units of the polypropylene chain length decreased the separation time.[18]

Solubilization

The solubilization of the water-soluble polyester surfactants applied with two synthesized dyes[15]

are shown in Figure 2. A linear relationship was obtained for the solubilization of the applied dyes with the concentration of the water-soluble polyester surfactants. The solubilization capacity of the water-soluble polyester surfactants increased gradually as the number of repeating units of polypropylene glycol increased. It is believed that the solubizate of dispersed dyes contained amino or carbonyl group and could associate with the polypropylene glycol units via hydrogen bonds.[23]

Dispersant Properties (Heat Stability)

Purified dispersed dyes are hydrophobic and almost insoluble in water. Their low aqueous solubility is attributed to hydrophobic bonding, causing aggregation and precipitation when the concentrations are increased. Generally, some surfactants (i.e, the dispersing agent) are incorporated during production of the final dye powder of liquid. Its function is to prevent aggregation and precipitation.[24] 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 a 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 four synthesized dyes: AβA (I): p-chlorobenzaldehyde aniline azo dye, AβA (II): p-hydroxybenzaldehyde aniline azo dye and ASA

Table VI   Dispersant Properties of Water-Soluble Polyester Surfactants Based on 1,4-Butane Diol (IP$_1$–IP$_5$) and 1,6-Hexane Diol (IIP$_1$–IIP$_5$)

Polyester	Dispersability			
	AβA (I) Dye	AβA (II) Dye	ASA (III) Dye	ASA (IV) Dye
IP$_1$	16.55	60.08	35.80	39.90
IP$_2$	18.45	24.09	52.20	53.76
IP$_3$	21.17	25.37	55.00	56.70
IP$_4$	23.85	28.89	56.80	60.30
IP$_5$	27.45	32.25	60.40	64.96
Blank	9.15	11.53	16.38	18.72
IIP$_1$	16.20	22.39	32.60	38.50
IIP$_2$	17.35	23.54	45.30	46.48
IIP$_3$	19.70	25.47	53.40	55.30
IIP$_4$	23.42	26.90	54.70	57.82
IIP$_5$	24.15	29.12	56.40	62.02
Blank	9.15	11.53	16.38	18.72

Table VII   Biodegradability Percent of Water-Soluble Polyester Surfactants Based on 1,4-Butane Diol (IP_1–IP_5) and 1,6-Hexane Diol (IIP_1–IIP_5)

Polyester	$F_1 + F_2$	1st Day	2nd Day	3rd Day	4th Day	5th Day	6th Day	7th Day
IP_1	5	63	71	78	86	92	96	—
IP_2	10	62	68	75	83	89	95	—
IP_3	15	59	65	74	80	86	91	98
IP_4	20	57	63	70	76	85	88	92
IP_5	25	52	58	60	76	78	82	89
IIP_1	5	60	69	76	84	90	93	—
IIP_2	10	58	64	73	81	87	88	96
IIP_3	15	57	67	70	77	82	85	94
IIP_4	20	53	58	59	73	79	84	90
IIP_5	25	51	56	57	59	76	79	84

(I): acetylacetone benzaldehyde aniline azo dye, and ASA (II): ethylacetoacetate-p-methoxy aniline azo dye. These systems[15] are shown in Table VI. From this table, it is clear that in all of the four applied dye systems, the heat stability was improved by the addition of the water-soluble polyester surfactants. For the same dye, the number of repeating units of polypropylene glycol of the polyester surfactants had only a slight influence on stability.

The high heat stability of the water-soluble polyester surfactants was probably caused by their unique structural features: (1) high MW, (2) the aromatic structure and ester linkage of the hydrophobic portion, and (3) the multiple ionic groups and polyoxypropylene chains of the hydrophilic portion. These structural features favor its adsorption onto the surface of dye crystals. The multisulfonate groups on the adsorbed dispersing molecules produce strong electrostatic repulsion and, hence, stabilize the dispersion.[25] However, the nonionic portion also stabilizes the dispersion, presumably because of its high hydrated polyoxypropylene chain extending into the solutions in the form of coils that present an excellent steric barrier to aggregation.[26] 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. At an 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.

Biodegradation

A biodegradation test in ordinary river water[27] gave satisfactory results, as shown in Table VII.

All the products had a degradation of about 80% after about 6 days. It is suggested that the polyoxyproplene chains became degraded by bacterial or enzyme hydrolysis with the propylene group converted to propylene glycol.

Biological Activity Test

The biological activity of the prepared polyesters were tested with the cup–plate method.[27] Their effectiveness against a number of microorganisms of important application to chemistry, industry agriculture, and medicine were tested with the aim of obtaining specific derivatives that could have potential in agriculture or in the chemical industry in addition to its application in the detergent field.

The microorganisms tested were gram-positive (*Bacillus cereus* and *Bacillus circulans*) and some fungal-plant pathogens (*Asperigillus niger* and *Penicillium notatum*).

The sensitivity of the selected microorganisms to some prepared polyesters was determined *in vitro* with criteria outlined in the experiment in the concentration range (125–500 mg/mL).

CONCLUSIONS

From these results and other previous data, we conclude that the introduction of the SO_3Na group in water-soluble surfactant moieties of the prepared polyesters increased their activity.

REFERENCES

1. Hsu, K. C.; Lee, Y. F.; Chiany, S. Y. J Appl Polym Sci 1995, 57, 1205.

2. Lin, S. Y. Text Chem Colorist 1981, 13, 261.

3. Cochin, D.; Laschewsky, A.; Nallet, F. Macromolecules 1997, 30, 2278.

4. Altwood, D.; Florence, A. T. Surfactant Systems; Chapman & Hall; London, 1983; p B-469.

5. Boyd, J.; Parkinson, C.; Sherman, P. J Colloid Interface Sci 1972, 41, 539.

6. Schmolka, I. R. J Am Oil Chem Soc 1977, 54, 110.

7. Sorenson, W. R.; Campbell, T. W. Preparative Methods of Polymer Chemistry; Wiley Interscience: New York, 1961; p 35.

8. Poutov, V. D.; Anufrieva, E. V.; Krakovyo, M. G. Chim J Polym Sci 1998, 16, 268.

9. Vogel, A. I. Textbook of Practical Organic Chemistry, 4th ed.; Longman: London 1987; pp 754, 1168.

10. Findly, A. Practical Physical Chemistry, 6th ed.; Longman: London, 1963; p 101.

11. Ross, J.; Milles, G. P. Oil Soap 1941, 18, 90.

12. Abe, N. Dyeing Ind 1979, 27, 331.

13. Elworthy, P. H.; Macfariance, C. B. J Pharm Pharmacol 1962, 14, 100.

14. Badder, F. G.; Nosseir, M. H.; Messiha, N. N.; Ikladious, N. E. Eur Polym J 1976, 12, 631.

15. Bird, C. I. J Soc Dyers Colour 1954, 70, 68.

16. Weihua, M.; Yigiang, Z.; Jun, C.; Shanknan, F.; Frank, J. Macromolecules 1999, 32, 528.

17. Bouvy, A. Eur Coat J 1996, 11, 3.

18. El-Sawy, A. A.; Mahmoud, A. A.; Shaher, N. O. J Serb Chem Soc 1990, 55, 395.

19. El-Sawy, A. A.; Esawy, A. S.; Sukkary, M. M.; Eissa, A. M. Hung J Ind Chem 1992, 20, 25.

20. El-Sukkary, M. M.; El-Dip, E.; El-Sawy, A. A. Hung J Ind Chem 1986, 14, 223.

21. Issa, I. M.; Issa, R. M.; Mahmoud, M. R.; Temerk, Y. M. J Phys Chem 1973, 235, 289.

22. Chen, K. M.; Liu, H. J. J Appl Polym Sci 1987, 34, 1979.

23. Jones, F. J Soc Dyers Colour 1984, 100, 66.

24. Finch, C. A. Chemistry and Technology of Water-Soluble Polyesters; Plenum: New York, 1981; p 233.

25. Osburn, Q. W.; Benedict, J. H. J Am Oil Chem Soc 1966, 43, 141.

26. Abouzeid, A. A.; Shehata, Y. M. Ind J Pharm 1969, 31, 72.

27. Eter, E.; Throck, M.; Richard, R. E.; David, A. J Am Oil Chem Soc 1974, 51, 486.