Synthesis and Surface Activity of Self-Sequestering Surfactants

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A novel series of self-sequestering surfactants has been synthesized by the reaction of phthalic anhydride, citric acid and polyethylene glycol. The unique structural features of these surfactants have been confirmed by infrared, nuclear magnetic resonance and elemental analysis. These surfactants exhibit excellent properties of self-sequestering. Besides good surfactant properties, including surface tension, low-foaming, emulsifying power and dispersant properties, they possess autonomous sequestering ability without any help of additional sequestering agent.

KEY WORDS: Citric acid, dispersant properties, emulsifying power, low-foaming, phthalic anhydride, polyethylene glycol, self-sequestering surfactant, sequestering power, surface activity, synthesis.

It is well known that in a hard water-surfactant system, the surface activities of surfactants are considerably reduced, due to the presence of multivalent ions in water (1). Certain materials, called sequestering agents, are added to avoid this disadvantage. Organic polycarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA) and inorganic salts, such as sodium tripolyphosphate (STPP), are good sequestering agents (2,3). A novel surfactant, namely a self-sequestering surfactant, also has been reported recently for such uses (4–6). Besides surfactant characteristics, it also possesses autonomous sequestering characteristics without the help of a different complexing compound. However, these investigations were centered on the development of self-sequestering surfactants used in laundering or other washing operations.

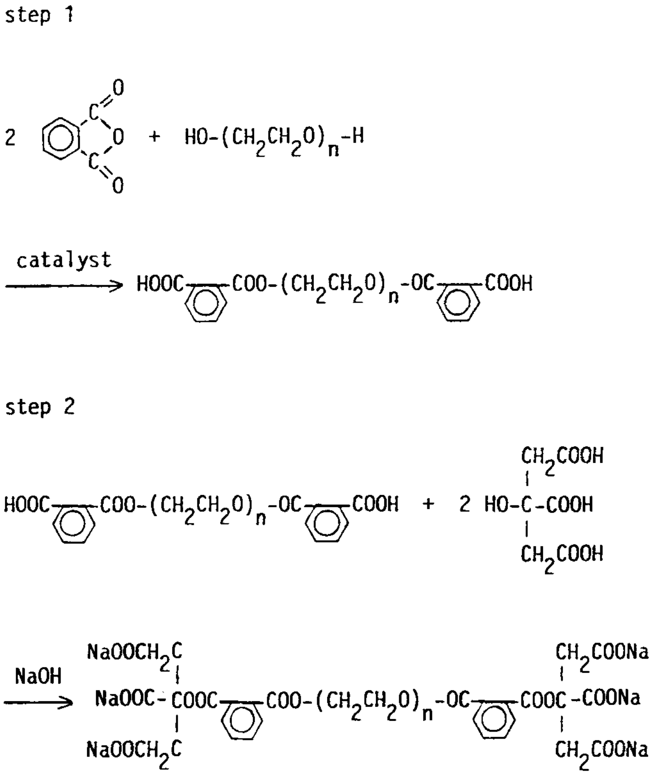
In many textile processes, such as dyeing of fibers, traces of multivalent ions may be responsible for faulty processes (1). It is often necessary to reduce the quantity of these ions by the addition of sequestering agents. Only limited information is available in regard to the use of self-sequestering surfactants for such textile processes.

In our previous studies, a series of water-soluble polyester surfactants prepared by the reaction of dicarboxylic acid and diol have been found to exhibit excellent surface-active properties (7–9). In the present study, a novel series of surfactants derived from these reported ester surfactants were prepared and used as self-sequestering surfactants for textile processes. These surfactants were synthesized by the reaction of phthalic anhydride (PA), citric acid (CA) and polyethylene glycol (PEG), and their properties of sequestering power, surface tension, foaming, emulsifying and dispersant power for disperse dyes were evaluated.

EXPERIMENTAL PROCEDURES

Materials. PA, CA, sodium isopropoxide and PEG with molecular weights from 200 (PEG 200) to 1000 (PEG 1000), purchased from Hayashi Pure Chemical Co. (Osaka, Japan), were all reagent-grade and used without further purification. Naphthalene sulfonate condensate, supplied by Saffron Chemical Co. (Taipei, Taiwan), and three disperse dyes, supplied by ICI Co. (Manchester, England), were commercial grade. The three disperse dyes used were Dispersol Red B-2B (C.I. Disperse Red 60), Dispersol Blue BR (C.I. Disperse Blue 56) and Dispersol Yellow B-6G (C.I. Disperse Yellow 218).

Synthesis of self-sequestering surfactants. The surfactants were prepared through two steps which are shown in Scheme 1.



SCHEME 1

The first step is reacting PA with PEG by the presence of a catalyst (titanium isopropoxide) at 240–250°C, and the second step is reacting the products obtained in the first step with CA at 180°C. Because the reaction of the second step is reversible, the formed water must be removed from the system continuously to maintain a forward direction of the reaction. The following example shows a typical recipe for preparing a self-sequestering surfactant involving MA, CA and PEG 200.

A reaction mixture containing 150 g (*ca.* 1 mol) of PA, 100 g (0.5 mol) of PEG and 3 mL of catalyst was stirred mechanically and heated to 240–250°C under a nitrogen atmosphere. The temperature was held there until the acid value of the product was below 60 (*ca.* 3 hr). The product was then cooled to 150°C and 192 g (1 mol) of CA was added. The mixture was reheated to 180°C under vacuum until 36 mL (*ca.* 2 mol) of water was trapped (*ca.* 3 hr).

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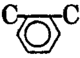
Then the product was cooled under nitrogen atmosphere and neutralized with sodium hydroxide solution.

The purification of products was carried out by ultrafiltration with a Spectra/Por MWCO 500 and 1000 membrane (nominal cutoffs, MW, 500 and 1000) (Spectrum Medical Co., Los Angeles, CA). The purity of the filtered products was confirmed by thin-layer chromatography (TLC) with methanol/chloroform/toluene (10:1:1) as eluting solvent. Four spots were observed in the samples before purification, and only one spot was observed in the samples after purification. After confirmation that only one component was present in the purified compounds, they were used for the analyses, surface-active properties and sequestering power measurements.

The appearance and yields of four self-sequestering surfactants synthesized in this study are shown in Table 1. All four surfactants are water-soluble—compound I and II are brown solids, and compound III and IV are brown liquids.

Analyses. The structure of the final products was confirmed by infrared (IR) and nuclear magnetic resonance (NMR) spectral analysis. IR spectra were obtained with a Japan Spectroscopic FT/IR-3 spectrophotometer (Japan Spectroscopic Co., Toyko, Japan) and NMR spectra were obtained with a Varian EM 360 L NMR spectrophotometer (Varian, Palo Alto, CA). IR spectra displayed bands at 3400 (O-H, intermolecular hydrogen bond), 2900 (C-H, methylene), 1730 (C=O), 1600, 1480 (C=C, ring stretch), 1580, 1430 (COO^-, carboxylate), 1280 (C-O-C, asymmetric), 1120 (C-O-C, symmetric) and 950, 840 cm^{-1} (C-H, out of plane) for all four surfactants. The proton NMR spectra of products gave further support to the assigned structure: δ 2.5($-CH_2-COO-$), 3.5 (CH_2-CH_2-O-), 4.1, 4.3 ($-CH_2-OOC-$), 7.5, 7.7 (-OOCCOO-).

Measurements. Surface tension was determined at room temperature with a Japan Kyowa Kaimenkagaku CBVP-A3 surface tensiometer (Kyowa Kaimenkagaku Co., Tokyo, Japan). Foaming properties were determined by the Ross-Miles method. Foam production was measured by the height of the foam initially produced, and foam stability was measured by the height after 3 min. Emulsifying power was determined according to the method described by Takashita *et al.* (5,6). Five mL of 0.1 g/L surfactant solution and 5 mL of oily material were mixed in a test tube. After 20 vigorous shakes, the tube was allowed to stand undisturbed until any separation of two phases appeared. The time until the separation of two phases appeared was used to estimate the emulsifying power of surfactants. Dispersant properties of the surfactants for disperse dyes was determined according to the method described in our previous papers (7,9). A 100-mL solution containing 0.1 g commercial disperse dye and 0.1 g dispersing agent was adjusted to pH 5.0 by adding an appropriate amount of acetic acid, and then the solution was heated to 130°C for 1 hr by a computer-controlled dyeing system. After this treatment, the solution was cooled to 90–95°C and vacuum filtered immediately through a Buchner funnel with Toyo No. 5A filter paper. The filtrate was diluted with acetone and the concentration was determined spectrophotometrically. The dispersibility was calculated as follows:

$$\text{Dispersibility}\ (\%) = \frac{\text{Dye concentration of filtrate}}{\text{Dye concentration of original solution}}$$

Sequestering power was determined by the sequestering ability of surfactants for calcium ion. A printing pH/MV meter and a calcium ion electrode (Ingold model HI 8418, Urdorf, Switzerland) were used to measure the equilibrium calcium ion concentrations. The standard calcium ion solution was freshly prepared by dissolving calcium chloride into a 0.003 M ammonium chloride/0.07 M ammonium hydroxide buffer solution, and the pH was adjusted to 9.70. The titrations were performed by adding the surfactant solution into a standard calcium ion solution in small increments, and the equilibrium free calcium ion concentrations were measured.

RESULTS AND DISCUSSION

Surface tension. Self-sequestering surfactants prepared in this study were observed to be of an amphipathic structure similar to traditional surfactants. The aromatic residues serve as the hydrophobic portion, and the carboxylic groups (anionic) and polyethylene chains (nonionic) are hydrophilic. The surface activity of these materials is shown in Figure 1. The surface tension of the solutions is reduced by addition of the surfactants. However, an abrupt inflection point in the curves, which corresponds to the critical micelle concentration (CMC) in the case of traditional surfactants, was not observed. Neither was such CMC phenomenon observed in our previous study (9). Increase in the length of the polyoxyethylene chain results in a decreased surface activity. This effect is similar to the results reported in our previous papers (7,9) and can be attributed to the fact that an increase in hydrophilicity of surfactants decreases the concentration of surfactants at the surface.

Foaming properties. Low foaming of surfactants is an important property in some recent applications, such as for dyeing auxiliaries in the modern textile dyeing industry. The relative low-foaming properties of self-

TABLE 1

Analyses of Self-Sequestering Surfactants

Compound	Mol. wt. of PEG used	Appearance	Mol. wt.	Yield (%)	Elemental analyses C (%) Found	C (%) Calcd.	H (%) Found	H (%) Calcd.
I	200	Brown solid	976.4	52.3	44.83	44.61	3.46	3.36
II	400	Brown solid	1176.4	85.5	46.28	46.30	4.60	4.34
III	600	Brown liquid	1376.4	83.4	47.50	47.49	5.82	5.04
IV	1000	Brown liquid	1776.4	79.9	49.88	49.08	6.51	5.97

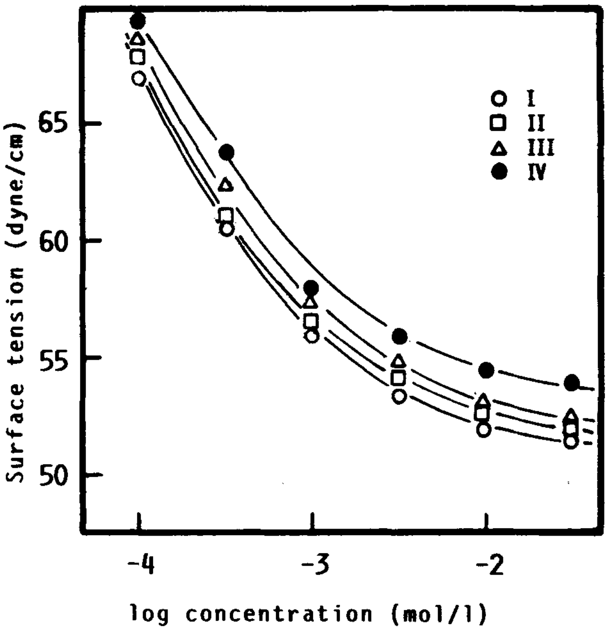


FIG. 1. Plots of surface tension *vs.* log molar concentration for self-sequestering surfactants at 25°C.

TABLE 3

Emulsifying Power of Self-Sequestering Surfactants

	Separation time (min)		
Compound	Liquid paraffin	Kerosene	o-Dichlorobenzene
I	7.83	15.33	8.15
II	6.75	10.50	10.20
III	5.67	8.60	8.33
IV	10.33	18.72	12.67

TABLE 4

Dispersant Properties of Self-Sequestering Surfactants

	Dispersibility (%)		
Compound	Red 60	Blue 56	Yellow 218
I	36.1	46.5	15.9
II	37.5	49.4	16.7
III	38.7	51.7	17.3
IV	39.1	53.2	17.9
Naphthalene sulfonate condensate	26.8	52.3	16.6
Blank	25.6	32.7	15.5

TABLE 2

Foaming Properties of Self-Sequestering Surfactants

	Foam height (mm)			
	30°C		85°C	
Compound	Initial	3 Min	Initial	3 Min
I	19	2	23	2
II	22	2	24	2
III	45	3	50	3
IV	50	4	57	4

sequestering surfactants are shown in Table 2. These four surfactants present not only low foaming, as measured by the height of the foam initially produced, but also low stability indicated by the height of the foam after 3 min. These low foaming effects, also described in our previous papers (7,9), probably are due to the presence of the many hydrophilic groups which cause a considerable increase in the area per molecule and produce less cohesive forces at the surface.

Emulsifying power. Emulsification is one of the most important properties of surfactants (10). In many textile processes, such as scouring and dyeing, it is necessary to introduce surfactants into the bath to remove oily impurities from the fibers. In these removal processes, the ability of surfactants to emulsify the oily impurities is important. The emulsifying ability of self-sequestering surfactants was estimated and is shown in Table 3. All four surfactants exhibit adequate emulsifying power for oils, as was expected.

Dispersant properties. In our previous studies, the water-soluble polyester surfactants, prepared from dicarboxylic acid and diol, exhibited excellent dispersant properties for disperse dyes (7,9). In this study, because of their amphipathic molecular structure similar to water-soluble polyester surfactants, we evaluated the dispersant properties of self-sequestering surfactants in three disperse dye systems and the results are shown in Table 4. It was found that for disperse dye systems the heat stability is improved by the addition of surfactants. However, the improvement is less pronounced than for surfactants prepared in our previous studies, due to the difference in: i) molecular weight; ii) multiple ionic groups; and iii) multiple polyoxyethylene chains. However, these products are better than traditional dispersing agents.

Sequestering power. As is known, a trace of multivalent ions may be responsible for faulty textile fabrication processes, such as dyeing of fibers. These ions can be introduced in the dyebath by textile fiber itself or from a carry-over from a previous process. Other important sources are inadequately purified water supplies and inadequate purity of the commercial chemicals used. With dyes, trivalent and divalent cations may form less soluble salts than those formed with sodium, leading to precipitation, or at least to aggregation of the dyes and to changes in shade (1). To prevent these problems, it may be necessary to remove the multivalent ions from the dyebath by adding sequestering agents during dyeing processes. In this study, the sequestering property of surfactants is evaluated by the determination of calcium ion sequestering power. The effect of the surfactant level on the free calcium ion concentration is shown in Figure 2. It is obvious that the surfactants prepared in this study have self-sequestering properties. Besides surfactant properties shown previously, they possess autonomous sequestering ability without the help of other added sequestering agents. The length of the polyoxyethylene chain of these surfactants has only a slight influence on their calcium ion sequestering power. This, as would be expected, is due to the sequestering ability of the end carboxylic groups of these surfactants.

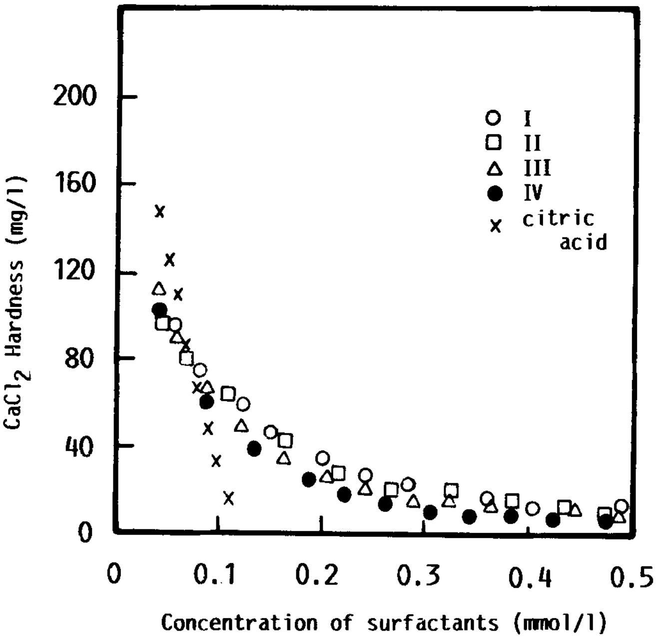


FIG. 2. Titration of calcium ions with self-sequestering surfactants and with citric acid.

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