

Preparation and Surface Activity of Water-Soluble Polyesters

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Synopsis

A novel series of water-soluble polyester surfactants has been prepared by the polymerization of SIPM, PA, and PEG. The unique structural features of these surfactants have been confirmed by IR and NMR analyses. These water-soluble polyester surfactants have been found to exhibit excellent surface active properties including surface tension, low-foaming, solubilization, and dispersant properties for disperse dyes.

INTRODUCTION

A surfactant is a substance that has a characteristic molecular structure consisting of a hydrophobic portion together with a polar or an ionic portion. When surfactant presents at 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, 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 a disperse or vat dye system;¹ the polysorbates exhibit excellent emulsifying properties for oil-in-water systems;^{2,3} and the polyoxyethylene-polyoxypropylene-polyoxyethylene block copolymers, known by their generic name as poloxamers, exhibit properties such as demulsification, dispersion, and emulsion stabilization.⁴

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

This paper describes the preparation and surface active properties of a series of novel water-soluble polyester surfactants. The surface active properties studied in this paper include surface tension, foaming, solubilization, and dispersant characteristics for disperse dyes.

EXPERIMENTAL

Materials

5-Sulfoisophthalic acid dimethyl ester sodium salt (SIPM) supplied by Sanyokasei Chemical Co. was a commercial grade, phthalic anhydride (PA), and titanium isopropoxide purchased from Hayashi Pure Chemical Co. were reagent grade. Polyethylene glycol (PEG), molecular weight from 106 (diethylene glycol, DEG) to 1000 (PEG 1000), were reagent grade and used without further purification. Naphthalene sulfonate condensate supplied by C. L. Chemical Co. was extracted with ethyl for 8 h and recrystallized twice from ether-methanol. All of other reagents were analytical grade and used without further purification. 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). These dyes supplied by I. C. I. Co. were recrystallized three times from ethanol and their purities were confirmed by the tests of thin layer chromatography (TLC).

Preparation of Water-Soluble Polyesters

The water soluble polyesters were prepared by two steps: the first step is reacting PEG with SIPM by the presence of catalyst (titanium isopropoxide) at 180–200°C, and the second step is reacting the products which obtained in the first step with PA at 240–250°C. Because the reactions are reversible, the methanol or water must be removed from the system continuously to maintain the reaction in forward direction. The following example shows a typical recipe for preparing a water-soluble polyester which involves PEG 400, SIPM, and PA.

A reaction mixture containing 400 g (1 mol) of PEG 400, 148 g (0.5 mol) of SIPM, and 1 g of catalyst was stirred mechanically and heated to 180–200°C under a nitrogen atmosphere. The temperature was held there until 39 mL (ca. 1 mol) of methanol was trapped. Next, 74 g (0.5 mol) of PA was added and the mixture was reheated to 240–250°C under a vacuum condition. The reaction was followed till 9 mL (ca. 0.5 mol) of water was trapped (ca. 3 h). Then the product was cooled under nitrogen.

Purification

The purification of products was carried out by ultrafiltration with a Spectra/Por MWCO 1000 membrane (nominal cutoff MW = 1000). The purity of purified water-soluble polyesters was confirmed by the tests of TLC. The TLC aluminum sheets (5 × 7.5 cm) precoated with silicagel 60F₂₅₄ of 0.2 mm layer thickness were used (Merck type 5549). Samples were spotted on the plates using fine capillary tubes. The eluting solvent of chloroform/toluene/methanol (13/1/1) was used to develop the plates. Four spots were observed in the samples before purification, and only one spot was observed in the samples after purification. It was confirmed that only one component presenting in the purified compounds which were used for the analyses and surface active properties measurements later.

Analyses

The acid value and hydroxyl values were determined by usual methods described elsewhere, and from these values the molecular weight of water-soluble polyesters was calculated.⁵ The sulfonate group (SO₃Na) content was determined by the method described in JIS, Y 3366.

Infrared (IR) spectra were obtained with a Perkin-Elmer 735 B spectrophotometer, and nuclear magnetic resonance (NMR) spectra were obtained with a Varian EM 360 L NMR spectrophotometer.

Measurement

Surface tension was determined at room temperature with a Fisher Douy-type interfacial tensiometer.

Foaming properties was determined by Ross-Mile method using a foam accumulate measuring system, while the foaming production was measured by the height of the foam initially produced. The foaming stability was measured by the height after 3 min.

Solubilization was measured by a usual method that shakes a 50 mL solution containing 40 mg of purified disperse dye and various concentrations of water-soluble polyesters for 48 h at 30°C. The insoluble dyes were filtered away through a glass filter, and solubilized dyes were extracted from filtrate by toluene and their concentrations were determined spectrophotometrically.⁶

Dispersant properties was determined by the following method. 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 appropriate amount of acetic acid. Then the solution was heated to 130°C by a computer controlled dying system for 1 h. After this treatment, the solution was cooled to 90–95°C and vacuum filtered immediately by using a Buchner funnel, through Toyo No.5A filter paper. The filtrate was diluted by acetone and determined their concentration spectrophotometrically. The dispersibility was calculated as follows:⁷

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

RESULTS AND DISCUSSION

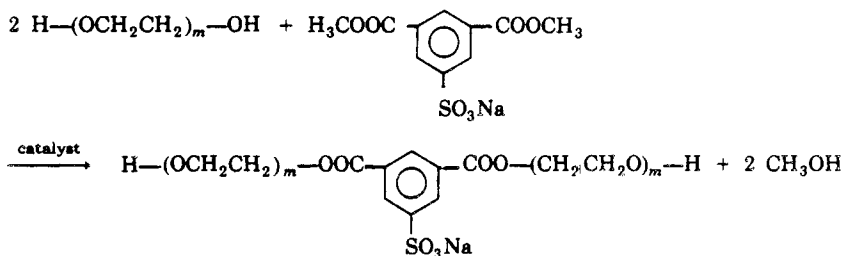
Preparation

The polymerization of SIPM, PA, and PEG can be represented as in Scheme 1:

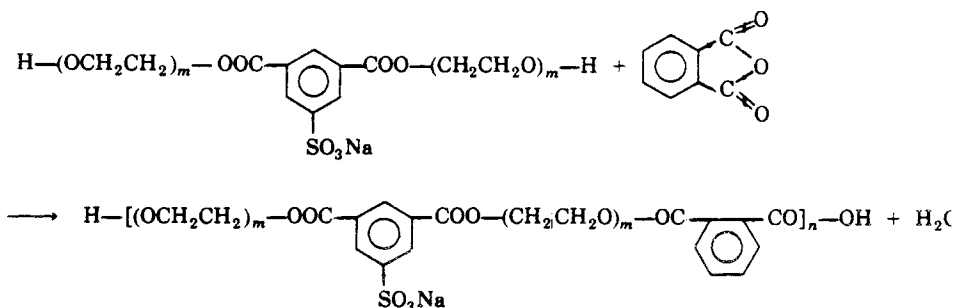
TABLE I
Analyses of Water-Soluble Polyester Surfactants

| Compound | Molecular weight of PEG used | Acid value | OH value | Molecular weight | Sulfate group content (%) |
|----------|------------------------------|------------|----------|------------------|---------------------------|
| I | 106 | 8.58 | 8.74 | 6474 | 13.63 |
| II | 150 | 8.36 | 8.40 | 6690 | 11.51 |
| III | 200 | 7.12 | 7.52 | 7665 | 9.97 |
| IV | 400 | 7.02 | 7.30 | 7825 | 6.70 |
| V | 600 | 6.92 | 6.56 | 8325 | 5.11 |
| VI | 1000 | 6.58 | 5.94 | 8961 | 3.74 |

Step 1



Step 2



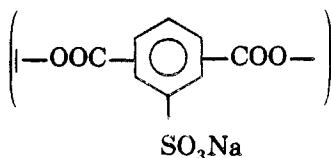
Scheme 1. Polymerization of SIPM, PA, and PEG.

The analyses of final products are shown in Table I. The molecular weight of PEG used in this study are from 106 (DEG) to 1000 (PEG 1000), and the molecular weight of the products are controlled between 6000 and 9000. All of the products are water-soluble, compounds I, II, III, and IV are brown solid and compounds V and VI are brown liquid in appearance. It is observed that the sulfonate group (SO_3Na) content decreased with the increase of the ethylene oxide chain length of PEG.

Figure 1 shows the IR spectra of these products. All of the IR spectra displayed bands at 3400 (O—H, intermolecular hydrogen bond), 3020 (C—H, aromatic), 2857 (C—H, methylene), 1620, 1597 (C=O, ring stretch), 1250 (C—O—C, asymmetric), 1050 (C—O—C, symmetric), 843, 760 (C—H, out of plane), and 1705 cm^{-1} (C=O). It is observed that the adsorption band at 2857 cm^{-1} (C—H, methylene) increased with the increase of the ethylene oxide chain length (from a to f).

The NMR spectra of these water soluble polyesters gave further support to the assigned structure, one of the examples showed in Figure 2 is the spectrum of compound IV. It gave signals at δ 3.5 ($-\text{CH}_2-\text{O}-$), 4.2 ($-\text{CH}_2-\text{COO}-$),

7.3 ($-\text{OOC}-\text{C}_6\text{H}_4-\text{COO}-$), and 8.3 ppm



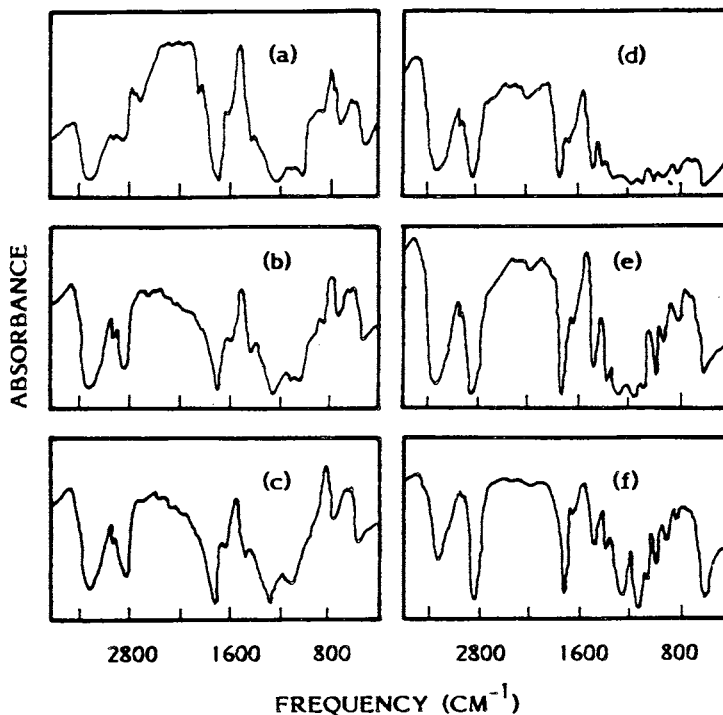


Fig. 1. IR adsorption spectra of water-soluble polyester surfactants: (a) compound I; (b) compound II; (c) compound III; (d) compound IV; (e) compound V; (f) compound VI.

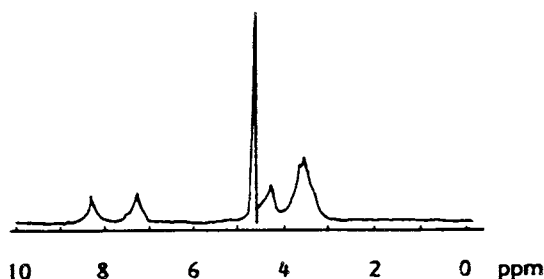


Fig. 2. Proton NMR of water-soluble polyester surfactants (compound IV).

Surface Tension

Water-soluble polyesters prepared in this study are observably of an amphipathic structure similar to the traditional surfactants. The aromatic residues are the hydrophobic portion, and the sulfonate group (anionic) and polyoxyethylene chain (nonionic) are the hydrophilic portion. The surface activity of these water-soluble polyester surfactants are shown in Figure 3. The surface tension of the solutions is reduced relatively by addition of the surfactants. It is due to the amphipathic structure causes concentration of the surfactant molecules at the surface and reduction of surface tension. Increase in the length of polyoxyethylene chain of nonionic portion results in a decreased surface activity clearly. This phenomenon is due to the increase of

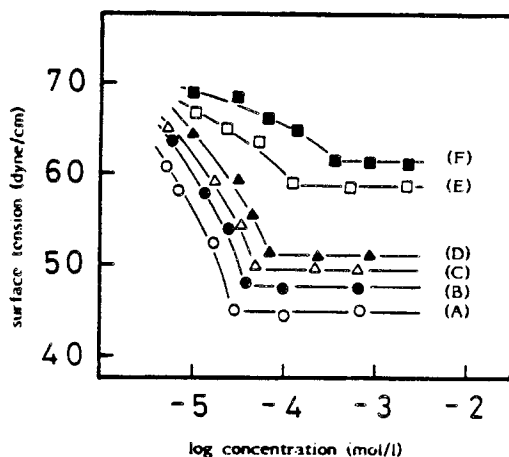


Fig. 3. Plots of surface tension vs. log molar concentration for water-soluble polyester surfactants at 25°C: (A) compound I; (B) compound II; (C) compound III; (D) compound IV; (E) compound V; (F) compound VI.

hydrophilic of surfactants makes the concentration of the surfactants at the surface decrease.⁸

The inflection point has been observed in the curves. The concentration at the inflection point corresponds to the critical micelle concentration (CMC) in the cases of traditional surfactants; however, it would be preferred to correspond to the maximum concentration of the surfactants at the surface in the cases of the polymeric surfactants, due to the presence of monomolecular micelles.⁹ The values are found smaller than the values of traditional surfactants, due to the high molecular weight and larger hydrophobic chain of water-soluble polyester surfactants. The values increase according to the increase in the length of polyoxyethylene chain of nonionic portion of surfactants (more hydrophilic).

The effects of electrolyte on the surface activity of water-soluble polyester surfactant solutions are shown in Figure 4. It is found that adding sodium chloride to surfactant solutions increases surface activity. The electrolyte presumably exerts its effect by decreasing the repulsion among the oriented ionic groups (SO_3Na) allowing a closer packing in the surface layer as the ionic strength is increased.¹⁰

Foaming Properties

The low-foaming tendency of surfactant has been an important property in some application recently, such as using it as a dyeing auxiliaries in the modern textile dyeing industry. The relative low-foaming properties of water soluble polyester surfactants are shown in Table II. All of these six products present not only the low-foaming production measured by the height of the foam initially produced, but also low-foaming stability, the height after 3 min. These low-foaming effects are probably due to (a) the presence of multihydrophilic groups causing a considerable increase in the area per molecule and producing less cohesive forces at the surface, (b) the multianionic hydrophilic

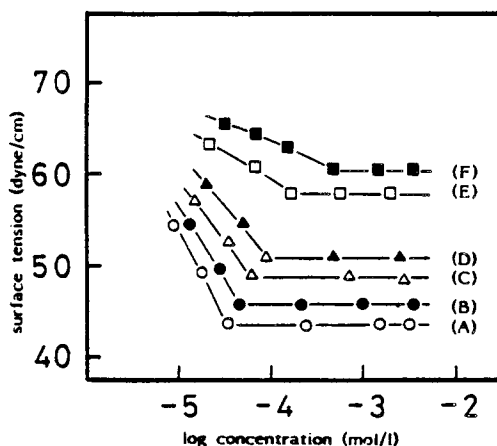


Fig. 4. Plots of surface tension vs. log molar concentration for water-soluble polyester surfactants in 0.2 M NaCl solutions at 25°C: (A) compound I; (B) compound II; (C) compound III; (D) compound IV; (E) compound V; (F) compound VI.

TABLE II
Foaming Properties of Water-Soluble Polyester Surfactants

| Surfactants | Foam height (mm) | | | |
|--------------|------------------|-------|---------|-------|
| | 30°C | | 85°C | |
| | Initial | 3 min | Initial | 3 min |
| Compound I | 9 | 0 | 12 | 0 |
| Compound II | 8 | 0 | 13 | 0 |
| Compound III | 9 | 0 | 13 | 0 |
| Compound IV | 10 | 0 | 15 | 0 |
| Compound V | 11 | 0 | 16 | 0 |
| Compound VI | 11 | 0 | 16 | 0 |

groups (SO_3Na) increasing the electrostatic repulsion among surfactant molecules counteracting the interchain cohesive forces, and (c) however, the water soluble polyesters which are believed to coil in the aqueous phase and decreasing the cohesive force due to intra- and intermolecular bond.

Solubilization

Solubilization is one of the important properties of surfactants. It may be defined as the spontaneous dissolving of an insoluble substance by reversible interaction with the micelles of surfactant in a solvent to form a thermodynamically stable isotropic solution.¹¹ In general, solubilization occurred only above the critical micelle concentration (CMC); above this, the amount of substance solubilized increase with the concentration of surfactant. However, the solubilization of water-soluble polyester surfactants for purified disperse dyes are observed different from traditional surfactants. One of the example is shown in Figure 5. A linear relationship is obtained for the solubilization of purified C. I. Disperse Blue 56 and the concentration of water-soluble polyester

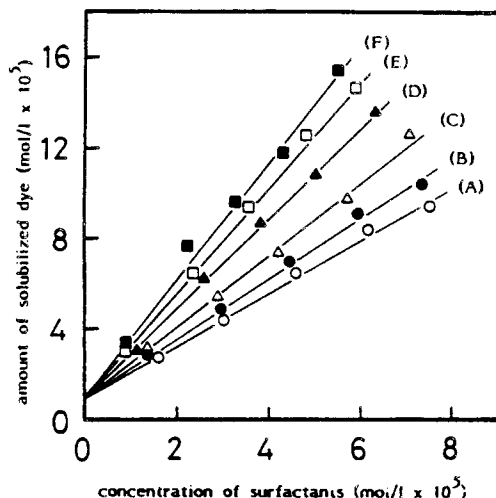


Fig. 5. Plots of amount of disperse dye solubilized as a function of concentration of surfactants: (A) compound I; (B) compound II; (C) compound III; (D) compound IV; (E) compound V; (F) compound VI.

surfactants. No such CMC phenomenon has occurred in the case of poloxamer surfactants,¹² and it is generally accepted that at lower concentrations these surfactants form monomolecular micelles and at higher concentrations these monomolecular micelles associate to form aggregates of varying size having the ability to solubilize disperse dyes.⁹ The solubilizing capacity of water-soluble polyester surfactants are observed increasing gradually as the polyoxyethylene chain length increases. It is believed that the solubilize of disperse dyes contain hydrogen-bonding amino or carbonyl group and can associate with the polyoxyethylene chains of surfactants.

Dispersant Properties (Heat Stability)

Purified disperse dyes are hydrophobic and almost insoluble in water.¹³ Their low aqueous solubility is attributed to hydrophobic bonding causing aggregation and precipitation when the concentration is increased. Generally, some surfactants (namely the dispersing agent) is incorporated during production of the final dye power or liquid. Its function is to prevent aggregation and precipitation of dye particles during application.¹⁴ However, in some practical dyeing processes, such as dyeing of polyester fibers at high temperature, the reaggregation of dye particles will occur at elevated temperature when the heat stability of the dispersant system is insufficient. For preventing this fault, an additional dispersing agent, having high heat stability, may be introduced into the dye bath initially or during the course of dyeing.^{1,14-16} Water-soluble polyester surfactants prepared in this study are observed properly to employ for these use and their stability at elevated temperature in three disperse dye systems are shown in Table III. It is clear that, in all of three disperse dye systems, the heat stability is improved by addition of water-soluble polyester surfactants and these improvements are observed to be larger than the traditional dispersing agent (naphthalene sulfonate con-

TABLE III
Dispersant Properties of Water-Soluble Polyester Surfactants

| Surfactants | Dispersibility (%) | | |
|-------------------------------------|--------------------|---------|------------|
| | Red 60 | Blue 56 | Yellow 218 |
| Compound I | 73.0 | 76.8 | 29.5 |
| Compound II | 59.2 | 63.7 | 29.5 |
| Compound III | 64.1 | 68.0 | 32.9 |
| Compound IV | 56.4 | 72.0 | 32.9 |
| Compound V | 68.5 | 64.3 | 29.8 |
| Compound VI | 64.1 | 61.3 | 36.2 |
| Naphthalene sulfonate condensate | 26.8 | 52.3 | 16.6 |
| Blank | 25.6 | 32.7 | 15.5 |

densate). For the same disperse dye, the length of polyoxyethylene chain of surfactants has only a slight influence on heat stability; however, the heat stability is observed to be much less for lower energy dye (less hydrophobic) such as C. I. Disperse Yellow 218 than high energy dye (more hydrophobic) such as C. I. Disperse Red 60 and Blue 56. This effect may be responsible for the difference of interaction between dispersing agents and dyes.

The high heat stability of water-soluble polyester surfactants is probably due to their unique structure feature: (a) high molecular weight, (b) aromatic structure and ester linkage of hydrophobic portion, and (c) multiple ionic groups and polyoxyethylene chains of hydrophilic portion. The high molecular weight, aromatic structure, and ester linkage of surfactants favor its adsorption onto the surface of dye crystals. The multisulfonate groups on the adsorbed dispersing molecules producing strong electrostatic repulsion, and hence stabilize the dispersion.¹⁵ On the other hand, the nonionic portion also leads to stabilize the dispersion presumably because of their high hydrated polyoxyethylene chain extending into the solutions in the form of coils that presents excellent steric barrier to aggregation.^{15,17} In both cases, the hydrophobic groups come into contact with the particle surface, leaving the hydrophilic groups directed toward the aqueous phase, and producing a solvation protection for dye particles. At an elevated temperature, the desorption of the novel dispersing agent from dye particles is minimized due to strong association between the dispersing agent and dye particles, thus resulting in high stability of these dispersant systems.

CONCLUSION

A novel series of water soluble polyester surfactants has been prepared by the polymerization of SIPM, PA, and PEG. Because of the unique structure features of these surfactants—high molecular weight, aromatic structure and ester linkage of hydrophobic portion, multiple ionic groups and polyoxyethylene chains of hydrophilic portion—these surfactants have been found to exhibit excellent surface active properties including surface tension, low-foaming, solubilization, and dispersant properties for disperse dyes.

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