Some Characteristics of Polyoxyethylene Sorbitol Tetra-Oleate: Oligomer Type Emulsifier

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ABSTRACT

Polyoxyethylene (P) sorbitol tetra-oleates with molecular weights of 2000 to 4000 were synthesized. They may be regarded as tetramers of those ordinary surfactants that consist of one hydrophilic and one hydrophobic group. Some emulsifying properties of the tetrameric surfactants were investigated including the phase inversion temperature (PIT, HLB-temperature). These surfactants are effective at relatively low concentration, they are stable for coalescence, and they are less irritating than conventional surfactants. Specifically, they proved to be good emulsifiers for unsaturated triglycerides such as olive oil. The mean droplet diameter of the emulsion was small, 1.5 microns. The emulsifying activity of these oligomer type surfactants for olive oil was improved markedly by the addition of 0.2-0.9 wt % of sodium oleate. Such effective performances of these surfactants have not been recognized in ordinary surfactants. It is expected that these oligomer type surfactants may find applications in various industrial fields.

INTRODUCTION

Nonionic surfactants that possess a hydrocarbon chain in one end of a molecule and a hydrophilic group on the other end of the molecule have been widely used. Surfactants that have more than two hydrocarbon chains as hydrophobic parts in a molecule, such as sucrose or sorbitol diesters (1-3), aerosols (4), and phosphate diesters (5,6) have been also used. If the surfactants containing one hydrocarbon chain in a molecule are regarded as monomer type surfactants, those containing two hydrocarbon chains in a molecule are dimers, and polyoxyethylene sorbitol tetra-oleate may be regarded as an oligomer type surfactant. Kuwamura studied the structural effects on the properties of nonionic surfactants having multi-chain structures (7,8). He concluded that the gross effects of the surfactants, such as emulsifying, dispersing, and wetting properties, were good if the hydrophobic portion possessed two hydrocarbon chains. The critical micelle concentration (CMC) of an oligomer type surfactant is generally lower than that of the corresponding monomer type surfactant because of its large molecular size or enthalpy of mixing (9). A good performance is expected for the oligomer type surfactant even at low concentration, and the emulsions made with it may

COMPONENT		FOUND wt.%	CALC. wt.%
$CH_2O(EO)_nCOR$ $CH\,O(EO)_nCOR$ $CH\,O(EO)_nCOR$ $CH\,O(EO)_nCOR$ $CH\,O(EO)_nH$ $CH_2O(EO)_nH$	POLYOXYETHYLENE (30) SORBITOL TETRA OLEATE	60.4	62.0
$HO(EO)_mCOR$	POLYETHYLENE GLYCOL OLEATE	34.1	33.5
RCOOH	OLEIC ACID	4.3	3.5
RCOONa	SODIUM OLEATE	1.2	1.0

$R: C_{17}H_{33}$ $EO: CH_2CH_2O$

FIG. 1. The chemical composition of ESTO-C type polyoxyethylene (30) sorbitol tetra-oleate.

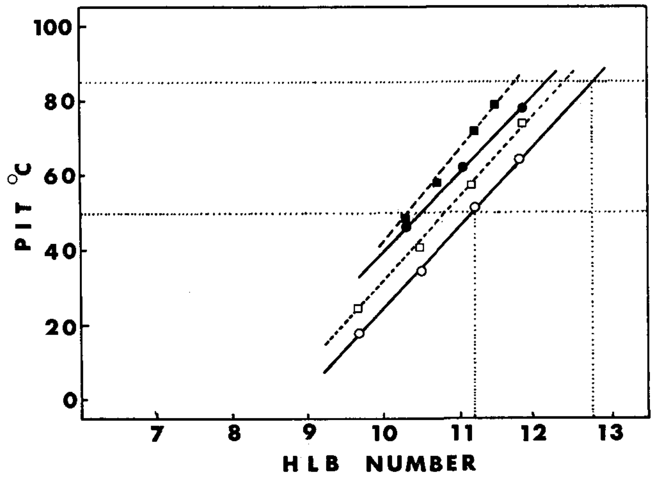

FIG. 2. The correlation between the HLB numbers of the surfactants and PITs of various emulsions stabilized with 5 wt % of surfactants. (—○—) ESTO-C/liquid paraffin system, (—●—) Polyoxyethylene (P) mono-oleate/liquid paraffin system, (- - □ - -) ESTO-C/Squalane system, (- - ■ - -) Polyoxyethylene (*p*) mono-oleate/squalane system.

TABLE I

The Relation between the Required HLB Numbers of Oils Obtained from the Emulsification Tests and the Optimum HLB Numbers Obtained from the PITs.

Oil	Liquid paraffin		Squalane		Hexadecyl 2-ethylhexanoate
Emulsifier	ESTO-C	POE (P) mono-oleate	ESTO-C	POE (P) mono-oleate	ESTO-C
Required HLB	10.0-12.8	10.2-11.5	9.4-12.7	10.6-11.6	9.5-13.5
Optimum HLB	11.2-12.8	10.4-12.1	10.7-12.5	10.5-11.6	10.8-12.5

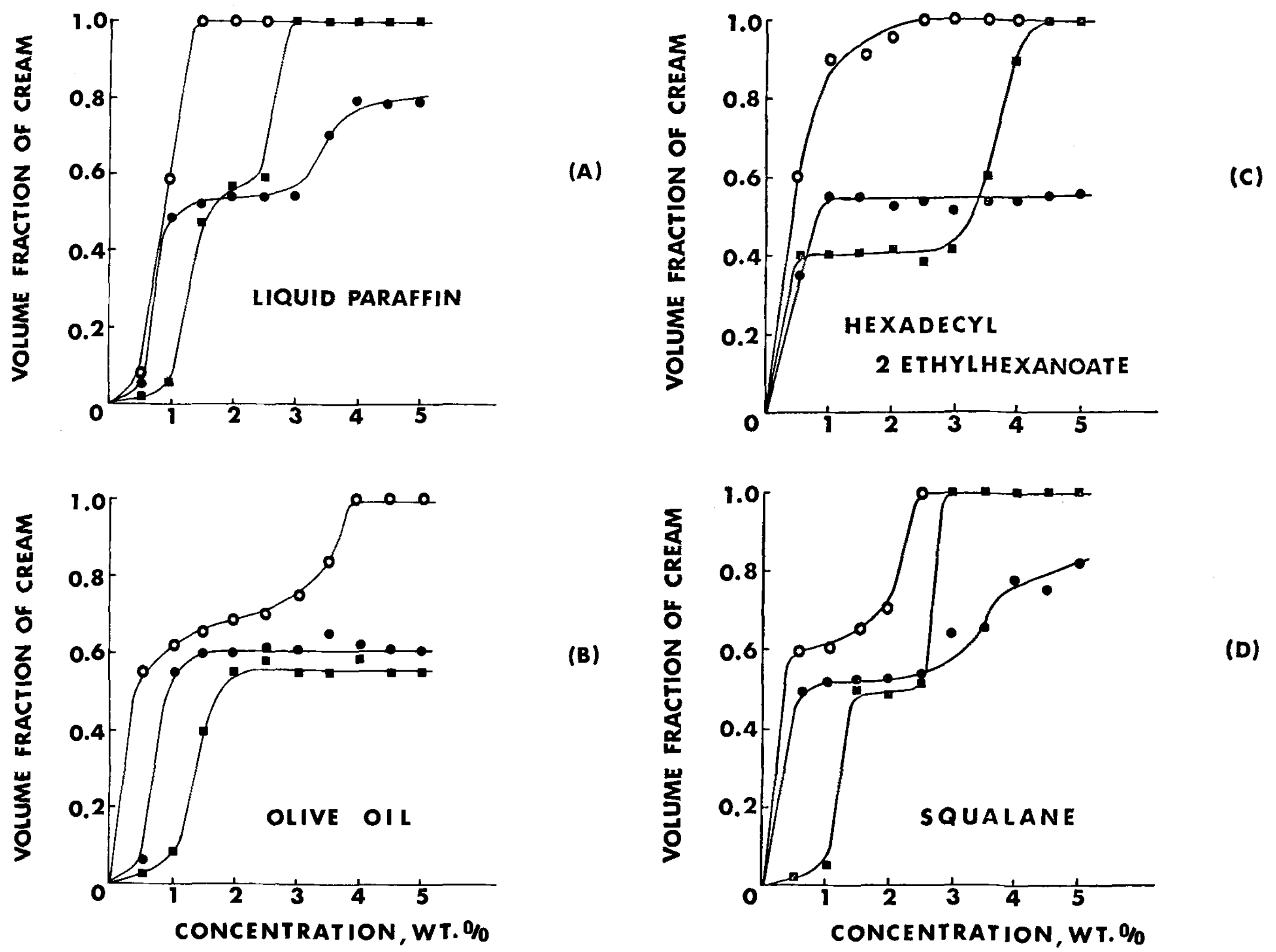

FIG. 3. The effect of the concentration of surfactants on the stability of the emulsions. (A): Liquid paraffin system. ○ : ESTO-C, P=40; ● : Polyoxyethylene (13) mono-oleate; ■ : Polyoxyethylene (20) sorbitan mono-oleate/sorbitan mono-oleate=53/47. (B): Olive oil system. ○ : ESTO-C,P=30, ● : Polyoxyethylene (10) mono-oleate, ■ : Polyoxyethylene (20) sorbitan mono-oleate/sorbitan mono-oleate=43/57. (C): Hexadecyl 2-ethylhexanoate system. (D): Squalane system. ○ : ESTO-C,P=40, ● : Polyoxyethylene (13) mono-oleate, ■ : Polyoxyethylene (20) sorbitan mono-oleate/sorbitan mono-oleate=53/47.

be stable against coalescence. Since the penetration of a surfactant into skin is inhibited by increased molecular weight (10), oligomer type surfactants with large molecular weights should be less irritating to human skin than monomeric surfactants. The present work was undertaken to investigate these properties of the oligomer type surfactants.

EXPERIMENTAL PROCEDURES

Materials

Polyoxyethylene sorbitol tetra-oleates were synthesized as follows. Ethylene oxide was added to an 85% aqueous solution of sorbitol in the presence of a small amount of sodium hydroxide as a catalyst at 125-135 C under 2-3 kg/cm^2 pressure. The products of the reaction contained 86.8, 90.8, 92.9, and 95.9 wt % of ethylene oxide, which corresponded to 20, 30, 40, and 60 oxyethylene units (P) in each product. Polyoxyethylene sorbitol and polyethyleneglycol were both obtained in this reaction. This mixture was esterified with oleic acid in the presence of sodium hydroxide at 220-230 C. The ester, called ESTO-C in this paper, was a mixture of polyoxyethylene sorbitol tetra-oleate and polyethyleneglycol oleate. In addition, it contained small amounts of free oleic acid and sodium oleate which were formed by reaction with the catalyst. The components of ESTO-C were fractionated by gel-permeation chromatography and were identified by chemical analysis. The results are shown in Figure 1.

To form pure oligomer type surfactant, ethylene oxide (264 g) was added to a mixture of dried sorbitol (182 g), dry xylene (200 ml), and metallic sodium (0.2 g) at 110 C under 2.5 kg/cm^2. After the evaporation of xylene and by-product polyethyleneglycol at 125 C under 0.05 mmHg, ethylene oxide (1056 g) was added at 130 C under 2-3 kg/cm^2. Polyoxyethylene sorbitol containing 87.9 wt % of ethylene oxide in a molecule (P=30) was obtained in this reaction. It was esterified with oleic acid using a small amount of sodium hydroxide as a catalyst. By-product sodium oleate was removed by an active clay. Polyoxyethylene sorbitol tetra-oleate, called ESTO-P in this paper, was obtained.

Commercial polyoxyethylene mono-oleate, sorbitan mono-oleate, and polyoxyethylene sorbitan mono-oleate were used for comparison without further purification, because the study was undertaken in connection with practical applications.

Methods

Phase inversion temperature (PIT): An emulsion containing 47.5 wt % of water, 47.5 wt % of oil, and 5 wt % of surfactant was prepared by shaking at 70 C. The electrical

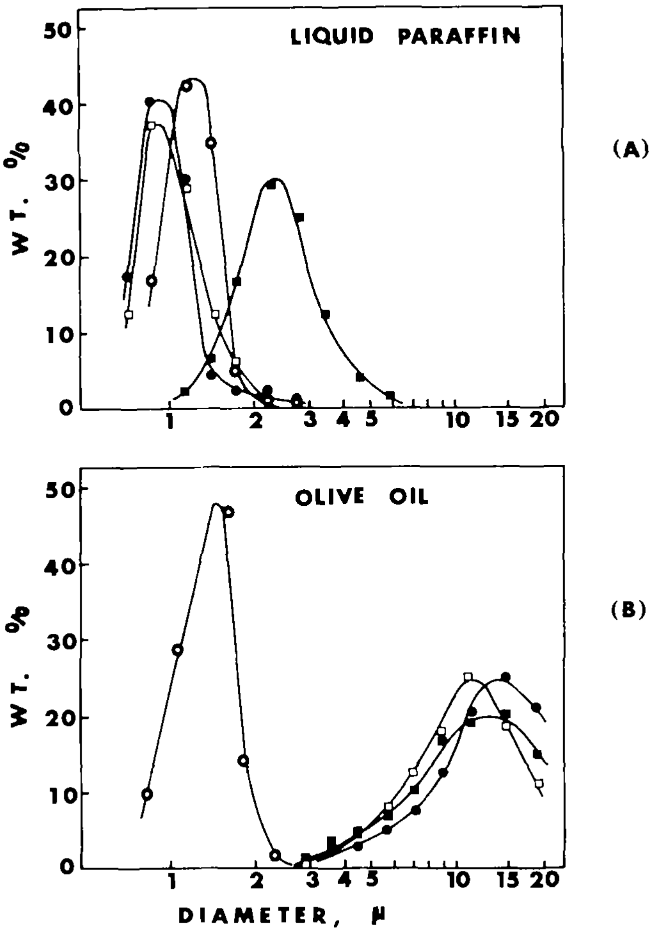

FIG. 4. Size distribution of emulsions. (A): Liquid paraffin system. ○ : ESTO-C,P=40, □ : ESTO-P, ● : Polyoxyethylene (13) mono-oleate, ■ : Polyoxyethylene (20) sorbitan mono-oleate/sorbitan mono-oleate=53/47. (B): Olive oil system. ○ : ESTO-C,P=30, □ : ESTO-P, ● : Polyoxyethylene (10) mono-oleate, ■ : Polyoxyethylene (20) sorbitan mono-oleate/sorbitan mono-oleate=43/57.

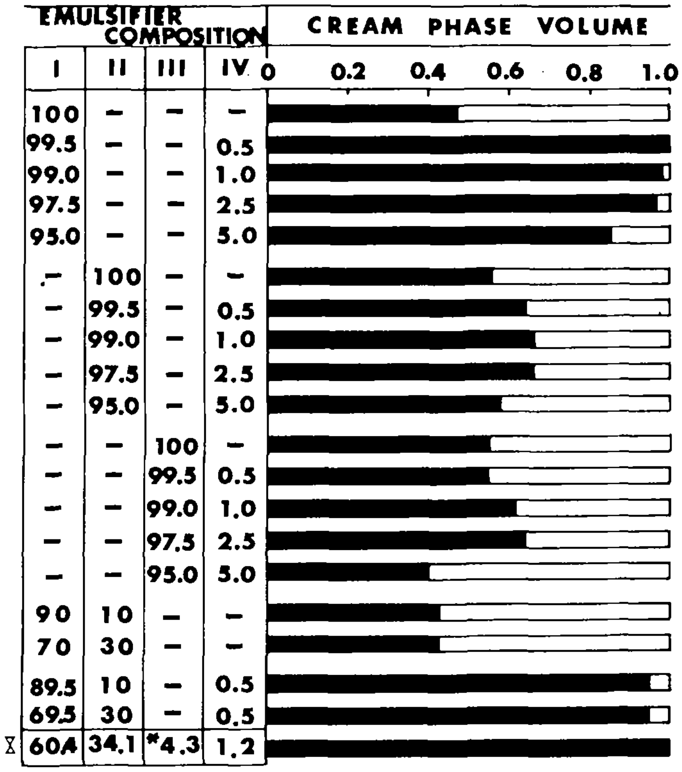

FIG. 5. The effect of the amount of sodium oleate in the surfactant on the stability of olive oil-water emulsions stabilized with 5 wt % of surfactants. ▭ : separated phase, ■ : o/w cream, I: ESTO-P, II: Polyoxyethylene (10) mono-oleate, III: Polyoxyethylene (20) sorbitan mono-oleate/sorbitan mono-oleate=43/57, IV: sodium oleate, * oleic acid, X : ESTO-C,P=30.

conductivity of the system was measured at slowly changing temperatures. The PIT of the system was conventionally determined by the point of inflection of the conductivity-temperature curve (11). The conductivity is very small, less than 1μυ/cm, when the oil phase is continuous, and large, more than 50μυ/cm, when water is the continuous phase.

Stability of emulsion: The stability of emulsions as a function of the concentration of the emulsifier was investigated by the following method. The mixture of oil and surfactant was placed in a 100 ml glass beaker and heated to 70 C. Water that had been heated to the same temperature was added slowly to the mixture with stirring. After the emulsion was cooled with agitation, it was poured into a test tube having an internal diameter of 15 mm. The emulsion was stored for 7 to 10 days at 25 C. Then the stability of the emulsion was determined from the volume fraction of separated phase.

Particle-size distribution: The emulsion was kept at 25 C for 24 hr. Then it was diluted 1,000-10,000 times with 0.9 wt % sodium chloride solution, and the size distribution of the emulsion was determined with a Coulter Counter Model ZB (12). The mean droplet diameter of the emulsion was calculated from the size distribution.

RESULTS AND DISCUSSION

Emulsifying Properties

PIT (13,14): The PITs in 1:1 mixtures of oil and water stabilized with 5 wt % of surfactants are shown in Figure 2. The HLB number of the oligomer type surfactant, calculated from its saponification number, was about 0.5-0.8 larger than that of the monomeric surfactant whose PIT was equal. This indicates that the oligomer type surfactant acts more hydrophobically than the monomeric surfactants in the emulsion system.

The relation between the PIT and the stability of the o/w type emulsion has been investigated by Shinoda and Saito. Emulsions are stable when they are stored at temperatures 25-60 C lower than their PIT (15,16). Therefore, emulsions having a PIT of 50-85 C would be stable when stored at 25 C, and the HLB number of the emulsifier having the same PIT as above may be the optimum HLB number to emulsify the oil. One can determine the required HLB number of an oil by making trial emulsions using emulsifier combinations that have different HLB numbers. The HLB number of the emulsifier that works best is the required HLB number of the oil (17). The correlation between the required HLB number of oils obtained from the emulsification tests and the optimum HLB number obtained from the PITs is summarized in Table I. The required HLB number of oil was taken as the HLB number of the emulsifier which gave a stable emulsion (no separation after 7 days at 25 C). The optimum HLB number was estimated from the PIT range of 50-85 C. The result indicated that the required HLB number and the optimum HLB number agreed with each other. This fact implies that the PIT measurements are directly applicable for evaluating the emulsifying performances of different surfactants.

It is evident from Table I that ESTO-C has a wider range of HLB numbers in which emulsions are stable than ordinary surfactants. This fact implies that ESTO-C is more adaptable to practical problems.

Stability of o/w emulsions: The effect of the concentration of emulsifier on the stability of emulsions composed of various oils is shown in Figure 3. The emulsifiers having the optimum PIT were used to emulsify each oil. It was found that ESTO-C was most effective at low concentration to emulsify each oil. This may have resulted from the low CMC value of ESTO-C. The CMC values of ESTO-C (P=30) and polyoxyethylene (5) mono-oleate from surface tension measurements were about 1.5 x 10^{-4} and 1.2 x 10^{-3} mole/liter respectively. This may be due to the larger heat of solution of ESTO-C than that of the monomeric surfactant. Emulsifying effects of ESTO-C on olive oil and hexadecyl 2-ethylhexanoate, both of which have relatively high polarity, were superior to those of the others. Practically, 4 wt % of ESTO-C yielded an excellent emulsion of olive oil. On the contrary, 40 vol % of coalesced or drained phase was observed in emulsions stabilized with 5 wt % of monomeric surfactants.

The size distributions of the emulsions stabilized with 5 wt % of each surfactant were measured with the Coulter Counter and are shown in Figure 4. There were no appreciable differences in the size distribution and the mean droplet diameter in liquid paraffin emulsions stabilized with different surfactants. On the other hand, the mean droplet diameter in the emulsion of olive oil stabilized with ESTO-C was 1.5 microns and the size distribution was sharp, whereas the mean droplet diameters of emulsions stabilized with the other surfactants were 5-8 microns and their size distributions were broad. It is clear from the data that only ESTO-C could stabilize the olive oil system. ESTO-P which is the pure oligomer type surfactant could not stabilize it.

Effect of different components on stability: Comparing the size distribution of the olive oil emulsion stabilized with ESTO-C and that stabilized with ESTO-P, it was supposed that the various components of ESTO-C took part in the emulsification of olive oil. In order to elucidate their contributions, the stability of olive oil emulsions emulsified by ESTO-P and by its separate components were investigated. The results are shown in Figure 5. Separated phase existed in the emulsion stabilized with 5 wt % of ESTO-P. The emulsion became very stable and there were no separated phases when 0.2-0.9 wt % of sodium oleate was added to the system. Such an effect of sodium oleate on the stability of emulsions was not observed in emulsions stabilized with ordinary surfactants. The stability of the olive oil emulsion stabilized with ESTO-P was depressed by adding more than 1.5 wt % of sodium oleate, possibly because the hydrophile-lipophile balance of the system became too hydrophilic by the addition of anionic surfactant.

Physiological Properties

The toxic and irritating properties of surfactants are important in the cosmetic and pharmaceutical fields. In a 24-hr closed patch test on human skin, ESTO-C exhibited no cutaneous reaction. Its irritancy was similar to that of ester type nonionic surfactants with low irritancy. The Draize method (18) showed this compound not to be an eye irritant. Its acute oral toxicity to rats was more than 40 g/kg in LD_{50} (Unpublished Life Science Research Laboratory data, 1974).

These findings indicated ESTO-C to be less toxic and irritating than familiar surfactants.

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[Received March 29, 1976]