the fractions with cocoa butter. The curve of the blend of mango fat and cocoa butter (product III) is closer to the curve of cocoa butter alone, but it lies on the other side and not in between the curves of the individual fats. Thus, mango fat is not fully compatible with cocoa butter. The deficiencies of the mango fat as such are compensated to some extent by the presence of cocoa butter.

Product II, in most respects, appears to be closer to cocoa butter than product I. However, the higher-melting product I may be more suitable in countries where atmospheric temperatures are higher than 30 C. This study indicates that fractionated mango fat can give solid fractions which may be successfully used as partial replacements for cocoa butter.

Because of the wide variation in the compositions of the fats from different mango varieties, however, the yields of the solid fractions having cocoa-butter-like properties are expected to vary considerably.

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Associative Structures of Polyglycerol Esters in Food Emulsions[1]

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ABSTRACT

Liquid crystalline types and the crystalline gel state of the commercially available tri- and octaglycerol esters are identified. The behavior of crystalline and liquid crystalline forms of these polyglycerol esters were studied in water dispersions, soybean oil and water emulsions, and in food emulsions. Triglycerol monoesters, primarily a mixed ester composition of palmitate and oleate, show hexagonal liquid crystalline activity as well as limited regions of stable α crystalline gels. Octaglycerol monostearate and monooleate primarily exhibit hexagonal liquid crystalline behavior which (below their Krafft point) form stable α-gels. A relationship between the associative structures and functional performance of these polyglycerol esters in food emulsions is presented.

INTRODUCTION

Polyglycerol esters (PGE) are versatile nonionic surfactants used primarily as food emulsifiers. They are composed of a mixture of predominantly linear glycerol polymers esterified with fatty acids or interesterified with triglycerides (1,2). Varying polymer length, type and degree of esterification of the PGE provides the basis for utility in product application by enabling the ester to match a desired hydrophilic-lipophilic balance (HLB) (1,3). Nevertheless, applications and acceptance have been limited, primarily because of PGE functional variability, inexplicable from the calculated HLB value.

Anomalies in the HLB approach are apparent when surfactant concentration, emulsion temperature and rela-

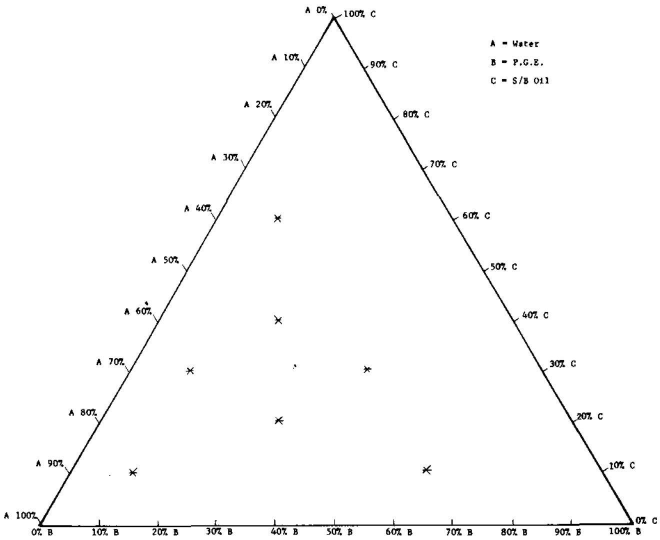

FIG. 1. Original data points.

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TABLE I

Polyglycerol Ester Characteristics

	PGE abbr.	Calcd. HLB	Apparent polyol MW	Primary fatty ester composition
Triglycerol monoshortening	3-HY	8.4	470	Palmitate, oleate
Triglycerol monoshortening	3-Lo	8.0	375	Palmitate, oleate
Octaglycerol monostearate	8-S	12.2	680	Stearate, palmitate
Octaglycerol monooleate	8-O	12.0	670	Oleate, linoleate

tively weak liquid-surfactant interactions are considered (4-6). Many surface-active lipids are known to have liquid crystalline activity from the amphiphilic properties of their molecules (7). Friberg et al. have demonstrated that the liquid crystalline mesophases give rise to a protective multilayer around the emulsion droplets, which increases their stability in retarding coalescense (8-10). Rheological and X-ray studies of absorbed emulsifier films at the oil-water interface have confirmed Friberg's findings (11). A similar water-emulsifier associative structure, described as the α crystalline gel, has been related to optimal aerating and starch complexing activity of monoglycerides (12).

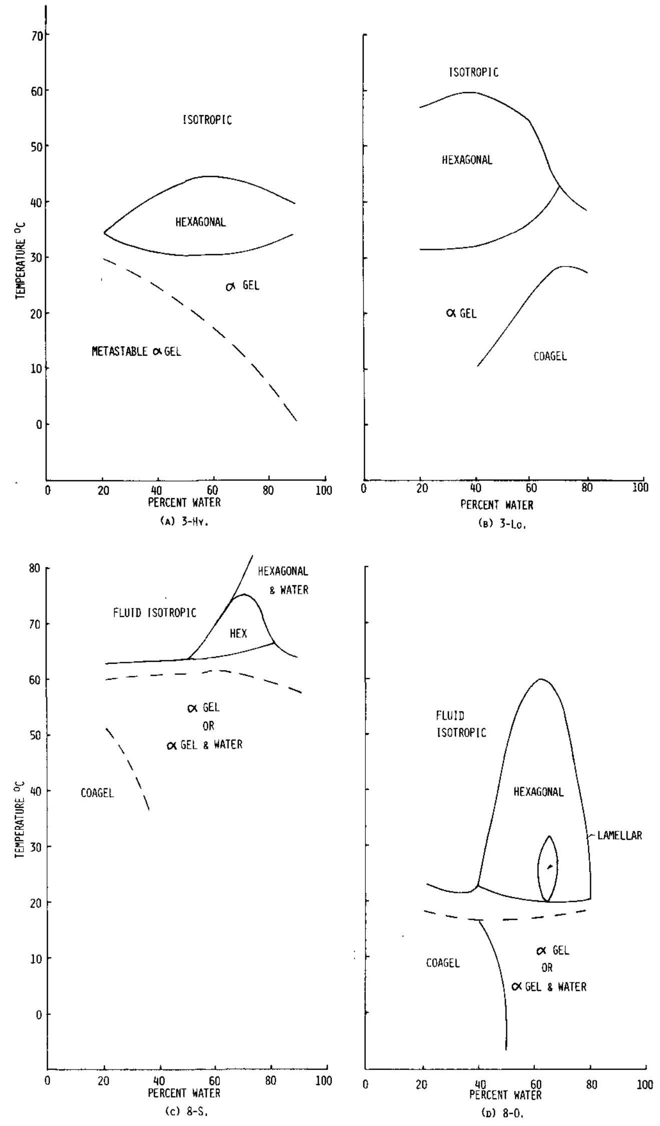


FIG. 2. Phase diagrams PGE-water binary systems.

The objectives of this work were to determine liquid crystalline and crystalline gel behaviors of four commercially available PGE in aqueous binary systems and in simple emulsions. Further, the relationship of these associated properties to food emulsions will be considered.

EXPERIMENTAL PROCEDURES

Materials

All PGE were commercially obtained products. Two triglycerol monoshortenings were from different commercial sources: Caprol 3GVS, Capital City Products, Columbus, OH, and Santone 3-1-SH, Durkee Foods Division, SCM Corp., Cleveland, OH. Octaglycerol monooleate and octaglycerol monostearate Santone 8-1-O and 8-1-S, also were from Durkee Foods. The soybean oil was refined, bleached, deodorized and the water deionized/distilled.

Equipment

A Bausch and Lomb polarized light microscope equipped with a Mettler FP52 heating/cooling stage was used to visually determine liquid crystalline and crystalline phases.

Sample Preparation and Analysis

PGE were mixed with water to form an aqueous dispersion. Five-g samples were prepared in a concentration range of 20-90% water at 10% intervals. Emulsions of PGE, water and soybean (S/B) oil were prepared quantitatively at concentrations indicated in Figure 1.

Attention was directed to the order of component addition when forming emulsions that incorporate the moderately hydrophilic triglycerol monoshortenings (Table I). Discrete response boundary analysis was used to estimate the phase boundaries of the emulsions. The different phases were assigned discrete numerical values and a full quadratic mixture model was fitted to these values via least squares estimation.

Polarized light microscopic analyses of the liquid crystalline and crystalline gel phases were made by introducing 10-20 mg of the prepared sample onto a prepared slide and sealing to avoid serious water loss at elevated temperatures. An enclosed sample reservoir ca. 0.30 mm thick was obtained.

RESULTS AND DISCUSSION

The four polyglycerol esters are characterized in Table I. The two triglycerol monoshortenings differ in the apparent molecular weight (MW) of their polyols. Apparent MW was calculated from the average MW of the polyol distribution, correcting for the low ratio of hydroxy number to formula weight for the cyclic polyol isomers. Santone 3-1-SH (3-Hy) has a greater apparent polyol MW than Caprol 3GVS (3-Lo). The fatty ester composition distinguishes Santone 8-1-S (8-S) from Santone 8-1-O (8-O).

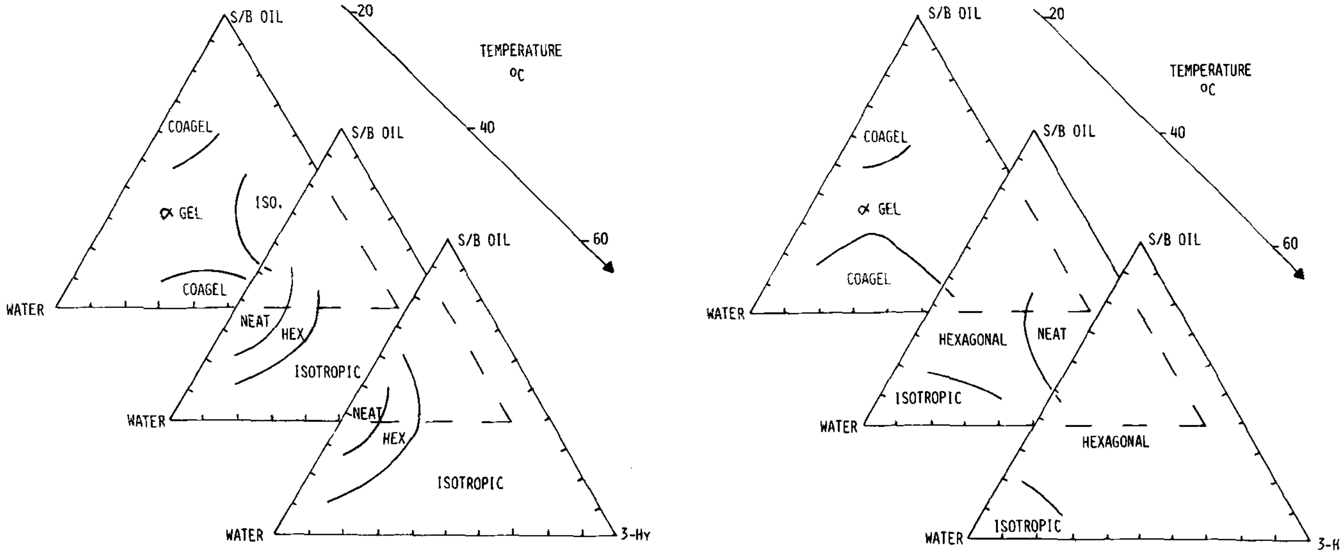
The phase diagrams of the PGE-water systems are given in Figure 2. Esters 3-Hy and 3-Lo exhibited liquid crystalline activity of the hexagonal type (Fig. 2, a and b). A hexagonal mesophase formed as a mixture of 3-Hy and water (20-90%) was heated to above the Krafft point of 30-35 C. The 3-Lo did not form liquid crystalline mesophses at high water concentrations, i.e., >70%. In the range of 20-60% water, 3-Lo and water retained liquid crystalline order up to temperatures of 55-60 C. Both 3-Hy and 3-Lo exhibited regions of stable α gels.

Esters 8-S and 8-O, having a more hydrophilic moiety, associated with water and formed liquid crystalline mesophases at high water concentrations (Fig. 2, c and d). The saturated fatty esters of 8-S form limited hexagonal mesophase upon heating to 62-65 C. The mesomorphic activity of 8-O is shifted to a lower temperature range because of its unsaturated fatty ester content. 8-S and 8-O associated with water as stable α-gels or α-gel-and-water dispersions at temperatures below their respective Krafft points.

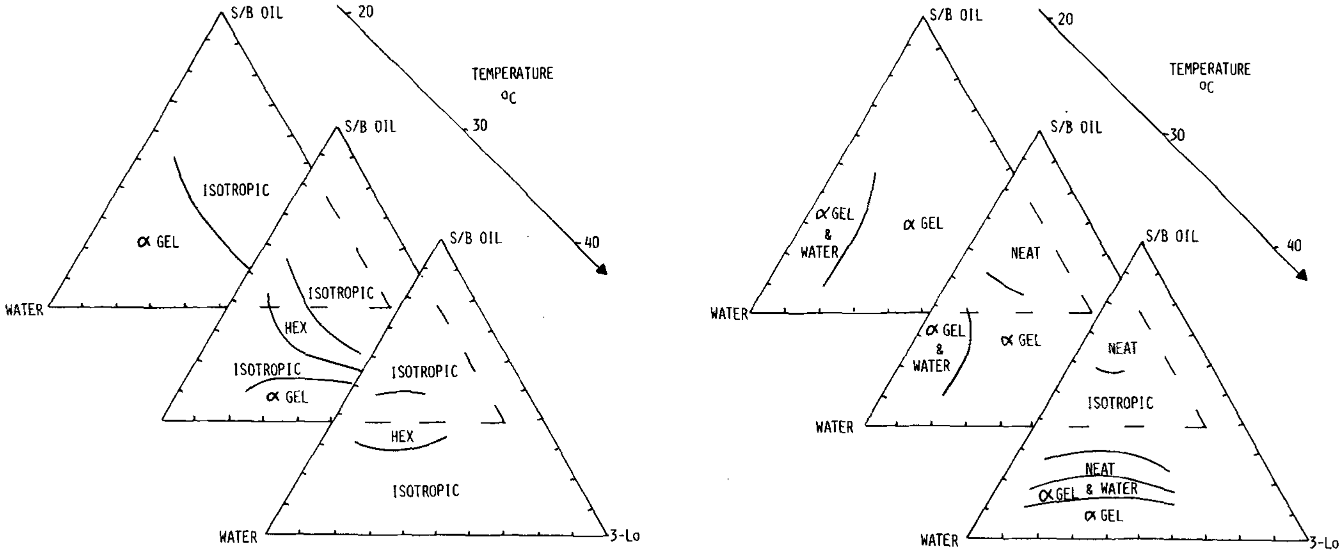
The phase behavior of PGE, water and S/B oil emulsions are depicted in the phase diagrams of the ternary systems (Figs. 3 and 4). This phase behavior, as with the binary PGE-water systems, is temperature-dependent. Temperature is included as a fourth function of the diagrams, projecting out of the plane of the page as the emulsion is heated. A comparison was made regarding the effect that the order of component addition had on crystalline and mesomorphic behavior of 3-Hy and 3-Lo. The phase behavior of the emulsions showed a significant change on reversing the order of component addition.

The response of the 3-Hy and 3-Lo emulsion to temperature increase was similar to that observed in the PGE-water system. 3-Hy retained mesomorphic structure to nearly 20 C above the isotropic melt of 3-Lo.

The formation of the functionally active lamellar/neat-type liquid crystals and stable α-gel at minimal PGE concentration appears related to the relative hydrophilic/hydrophobic character of the triglycerol monoshortenings. 3-Hy, slightly more hydrophilic than 3-Lo, formed a neat mesophase and crystallized to a stable α-gel upon initial dispersion in water at 10-20% concentration of 3-Hy (Fig. 3a). In contrast, 3-Lo formed a neat mesophase and stable α-gel at 10-20% concentration after initially being dispersed in oil (Fig. 3d).

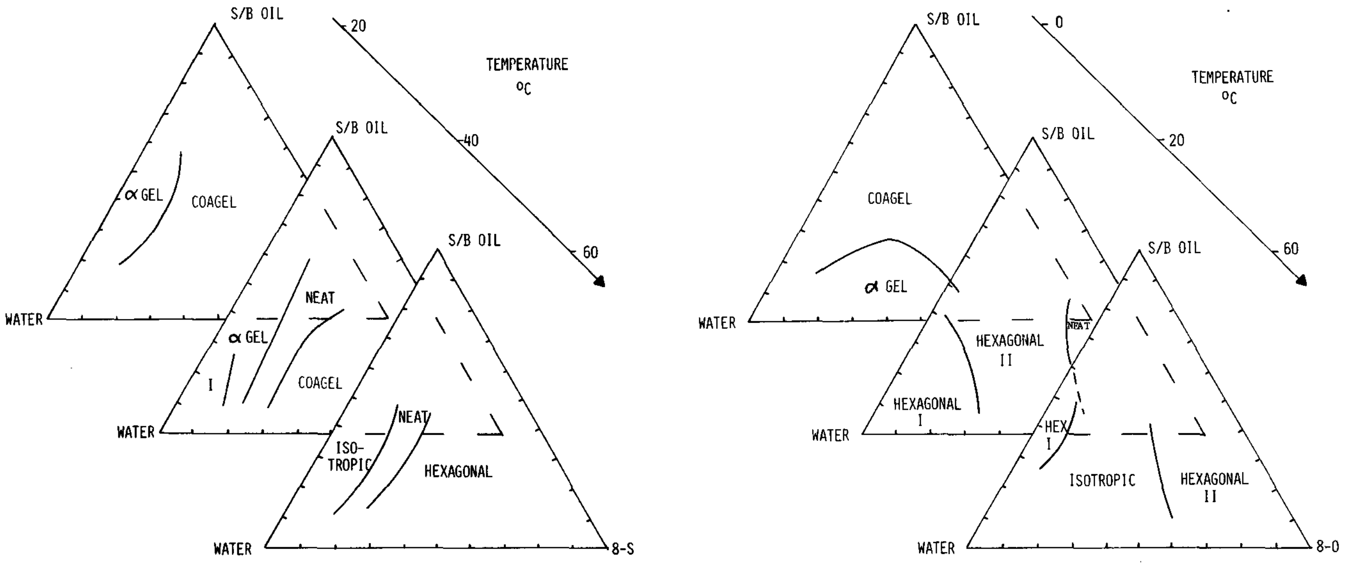


(A) 3-Hy → WATER → S/B OIL.   (B) 3-Hy → S/B OIL → WATER.



(C) 3-Lo → WATER → S/B OIL.   (D) 3-Lo → S/B OIL → WATER.

FIG. 3. Phase diagrams PGE, water, soybean (S/B) oil. Comparison of the order of component addition.



(A) 8-S → WATER → S/B OIL.

(B) 8-O → WATER → S/B OIL.

FIG. 4. Phase diagrams PGE, water, soybean (S/B) oil.

The relatively hydrophilic 8-S and 8-O were dispersed in water when the ternary emulsion systems were prepared (Fig. 4). Lamellar/neat liquid crystalline and crystalline gel order occurred in the 8-S emulsion at greater oil concentrations than those of 8-O.

The role of the associative properties of PGE relative to their functional performance in food emulsions was evaluated. 3-Hy and 3-Lo functional activity was evaluated in a yellow cake application. 8-S and 8-O were compared in whipped topping and ice cream applications.

A single-stage, mix yellow cake formula was used (Table II). 3-Hy and 3-Lo were evaluated separately, either dispersed in the shortening or incorporated as stable α-gel emulsions. The control formula was an industry-accepted emulsified shortening containing Polysorbate 60 and monoglycerides. Cakes prepared from formulations containing stable α-gels were scored overall superior to the control on external and internal cake appearance for a maximum of 65 (Table III) by a five-member panel. The shortening-dispersed 3-Hy performance was rated slightly inferior and the 3-Lo performance equal to the control.

Both polyglycerol esters appear to impart optimal activity when introduced into the cake formula in the α-gel state. This agrees with previously reported findings on the functional behavior of monoglycerides (12). The acceptable activity of the shortening-dispersed 3-Lo can be interpreted from the ternary phase diagram, Figure 3d. 3-Lo associates into a mesophase and stable α-gel in the emulsion when dispersed in oil prior to water addition. Essentially, the same order of ingredient addition is encountered when forming a cake emulsion.

8-S and 8-O were individually incorporated into a

TABLE II

High-Ratio Yellow Cake Formulation

Baker's percent	Ingredient
100	Cake flour
130	Sugar
50	Shortening w/emulsifier(s)
10	Milk solids
3	Salt
7	Baking powder
60	Liquid whole eggs
110	Water

TABLE III

Evaluation of PGE in Single-Mix Yellow Cake

		PGE 3-Hy		PGE 3-Lo	
	Polysorbate 60	Shortening dispersed	Stable α-gel	Shortening dispersed	Stable α-gel
Concentration (% shortening)	0.2	3.0	1.0	3.0	2.0
Monoglyceride (% shortening)	4.0	2.0	–	2.0	–
Specific volume cake (ml/g)	3.21	3.10	3.25	3.18	3.15
Overall score of cake (max 65)	52	45	55	51	58

TABLE IV

Fluid Whipped Topping Formulation

Percent	Ingredient
30.0	Vegetable fat
10.0	Sugar
2.0	Sodium caseinate
0.5	Cellulose gum
0.3	Emulsifier
Balance	Water

TABLE V

Evaluation of PGE in Fluid Whipped Toppings

	Polysorbate 60	PGE 8-O	PGE 8-S
Concentration (%)	0.3	0.3	0.3
Separation (cm) following first freeze/thaw cycle	2.5	Emulsion broke	2.0
Whip time (min)	12.00		10.75
Appearance	Firm, sl. curdy		Creamy, smooth

TABLE VI

Ice Cream Formulation

Percent	Ingredient
10.0	Milk fat (from 36% milk fat cream)
12.0	Sugar
5.0	Corn syrup solids
10.0	Nonfat milk solids
0.15	Stabilizer
0.15	Emulsifier
Balance	Water

TABLE VII

Evaluation of Polyglycerol Esters in Ice Cream

	Polysorbate 80	PGE 8-O	PGE 8-S
Concentration (%)	0.03	0.03	0.03
Mono/diglyceride (%)	0.12	0.12	0.12
Whipping time to obtain 100% overrun (min)	9.0	7.5	6.6
Meltdown—serum collected after 60 min at ambient temp. (ml)	6.0	7.0	10.5
Appearance during meltdown	Fair, dry, stiff	Good, creamy stiff	Fair, creamy stiff

nondairy, fluid, whipped topping formula which contained 30% fat (Table IV). The control contained Polysorbate 60. Each fluid topping was subjected to one freeze/thaw cycle prior to whipping. 8-O did not retain a stable fluid emulsion following the freeze/thaw cycle (Table V). 8-S functioned similar to Polysorbate 60.

A similar type of emulsifying activity of 8-S and 8-O was evaluated in a standard ice cream mix containing 10% fat (Table VI). Comparisons were made to a control containing Polysorbate 80. 8-O performed equal to the control with desired reduction in whipping time and a preferred creamy, firm appearance during meltdown (Table VII). 8-S was slightly inferior to the control having increased serum separation and a weak appearance during meltdown.

A comparison of the two applications just described for 8-S and 8-O illustrates the paramount roles of temperature and fat content. The temperature range providing stable crystalline/liquid crystalline structure must be within the range the emulsion will encounter. 8-O was unable to provide extensive structure above 0-4 C at the oil-water interface of an emulsion containing 30% oil (Fig. 4b). This was evident in the fluid whipped topping emulsion containing 8-O. In the lower-fat-containing frozen ice cream emulsion, 8-O provided excellent aerating and textural properties. In emulsions containing a moderate fat content of 20-70%, 8-S provided ordered interfacial structure and hindered excessive coalescence (Fig. 4a). This behavior of 8-S was observed in the fluid whipped topping application. At low fat, low temperature conditions (as in ice cream), 8-S transforms to a suspension of crystals plus water, i.e., a coagel, destabilizing the emulsion.

The functional properties of polyglycerol esters are largely predicted from their liquid crystalline and crystalline associative properties at the emulsion interface. Use of the technique of phase analysis improves precision and accuracy in predicting end use application for polyglycerol esters.

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