

Emulsification Properties of Polyesters and Sucrose Ester Blends I: Carbohydrate Fatty Acid Polyesters

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A number of carbohydrate fatty acid polyesters, potential fat substitutes, were screened for their ability to reduce surface and interfacial tensions alone or as blends with commercial emulsifiers. Commercial sucrose ester emulsifiers (Ryoto, Mitsubishi-Kasei Food Corporation, Tokyo, Japan) were evaluated alone or blended with other sucrose esters or with other carbohydrate fatty acid polyesters, and their surfactant properties were examined in terms of their ability to reduce surface and interfacial tensions at different concentrations and to stabilize oil-in-water (o/w) and water-in-oil (w/o) food emulsions at room and refrigeration temperatures, respectively.

In general, when used alone the carbohydrate polyesters were excellent stabilizers of w/o emulsions and poor stabilizers of o/w emulsions. Blending lipophilic carbohydrate polyesters with hydrophilic commercial emulsifiers, such as S-1670, produced stable o/w emulsions and unstable w/o emulsions. Our results suggest that emulsifier blends of potential fat substitutes with FDA-approved commercial sugar ester emulsifiers can be prepared for possible use in low-calorie foods, cosmetics and pharmaceuticals as o/w and w/o emulsifiers.

KEY WORDS: Carbohydrate fatty acid polyesters, emulsifiers, sucrose esters, surface activity.

The food industry has recently focused attention on the possible use of carbohydrate polyesters as fat substitutes in formulating food products (1,2). The use of surface-active agents (surfactants) has been shown to improve the finished quality of a number of foods. Various sucrose esters of varying hydrophile-lipophile balance (HLB 1-16) have been utilized in bread making and production of cookies (3-6). The emulsifiers were used to improve bread volume and texture, to extend shelf-life, and to control cookie spread factor (3,4,7).

Various food products, such as butter, low fat spreads, shortening, chocolate, and margarine are water-in-oil (w/o) emulsions and require emulsifiers to prevent separation. Akoh and Swanson (8-10) suggested that carbohydrate polyesters, such as raffinose and sucrose polyesters, may be suitable w/o emulsifiers based on their low HLB values (HLB 2-6). These carbohydrate polyesters, along with sorbitol and trehalose polyoleate (9), are lipophilic and may promote w/o emulsions. The degree of solubility of surfactants in water often suggests approximate HLB values and potential usefulness. However, the selection of an appropriate emulsifier or emulsifier combination for a particular food product must be determined experimentally. The most suitable carbohydrate polyester for food use is selected to acquire the desired physical properties of the finished product.

Since HLB values are algebraically additive, a blend of

emulsifiers, for example, carbohydrate polyesters and Ryoto sugar esters), needed to produce maximum oil-in-water (o/w) or w/o emulsion stabilities, can be designed. To date, there is no report describing the effect of blending carbohydrate polyesters with commercial emulsifiers, or of carbohydrate polyesters alone in reducing surface and interfacial tensions or increasing emulsion stability. Mixtures of lipophilic and hydrophilic emulsifiers often produce better and more stable emulsions than individual emulsifiers (11).

The objectives of this investigation were to evaluate the potential of carbohydrate polyesters, fat substitutes and their blends with commercial emulsifiers to reduce surface and interfacial tensions and to stabilize emulsions.

MATERIALS AND METHODS

Materials. Ryoto sugar esters (S-170 through S-1670) were supplied by Mitsubishi-Kasei Food Corporation (Tokyo, Japan). Xylene was purchased from Fisher Scientific (Norcross, GA). Alphadim 90AB (90% monoglyceride), a high-purity distilled monoglyceride, was supplied by American Ingredients Company (Kansas City, MO). Crisco vegetable oil was purchased locally. Synthesis and purification of carbohydrate polyesters, such as sucrose polyoleate, trehalose and sorbitol polyoleate, and raffinose polyester followed the procedures of Akoh and Swanson (8,10,12).

Measurement of surface and interfacial tensions. Surface tension was measured in distilled water at room temperature (25°C) with a CSC-DuNouy Interfacial Tensiometer Model 70545 (CSC Scientific Company, Fairfax, VA) (13). A platinum ring was immersed in water or in water containing a known concentration of emulsifier. The vessel containing the emulsifier solution was lowered while simultaneously increasing the torsion on the ring. The force (dynes/cm) required to detach the ring from the surface was taken as the apparent surface tension. True surface tension was obtained by applying correction factors.

The interfacial tension between water and xylene at 25°C was obtained with the same DuNouy Tensiometer described above. The platinum ring was immersed in a beaker of water and xylene or in an emulsifier solution in xylene gently placed on top of the water. The beaker containing the solution was lowered while simultaneously increasing the torsion on the wire. The force (dynes/cm) required to detach the ring from the interface was read directly from the dial as the apparent interfacial tension. The true interfacial tension was obtained after applying appropriate correction factors.

Measurement of food emulsion stability. The ability of the emulsifiers to stabilize o/w emulsions at room temperature was evaluated at 0.5% emulsifier concentration and 10% vegetable oil concentration. A solution of emulsifier in distilled water was placed in a Waring blender and mixed at low speed while slowly adding Crisco vegetable oil. The mixture was blended for 2 min and the food emulsion formed was transferred to a 100-mL graduated

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cylinder and held at room temperature. The volume of aqueous phase separated at the bottom at 0, 2, 4, 8, 12, 24 and 48 hr was measured. All measurements were in duplicate. Percent separation was calculated from the volume of oil added and the amount separated over a given period:

$$\frac{\text{Volume oil phase separated} \times 100}{\text{Total volume oil added}}$$

The control contained no emulsifier.

Water-in-oil emulsions were prepared by heating 0.5% emulsifier in vegetable oil at 70°C. The solution was allowed to cool to 25°C. The oil-emulsifier solution was placed in a Waring blender and mixed at low speed while 10% distilled water was slowly added. Blending was continued for 2 min. The food emulsion formed was transferred to a 100-mL graduated cylinder and stored in the refrigerator (4°C). The stability of w/o emulsions was determined at 0, 2, 4, 8, 12, 24 and 48 hr of storage by measuring the volume of aqueous phase separated at the bottom. All tests were in duplicate. Appropriate controls of vegetable oil and water with no emulsifier were used.

RESULTS AND DISCUSSION

Surface and interfacial tensions. Table 1 illustrates the effect of various carbohydrate fatty acid polyesters on the reduction of surface and interfacial tensions at 0.1% emulsifier concentrations, respectively. The HLB of the

commercial Ryoto sugar esters (14), the carbohydrate polyesters (8–10), and the weighted average HLB values of blended emulsifiers are also shown in Table 1. These experiments were carried out to screen the various emulsifiers prior to selecting some emulsifiers for further examination of their surface and interfacial tension reducing ability and their ability to stabilize o/w or w/o emulsions. Reduction of surface and interfacial tension is one of the most commonly measured properties of surfactants in solution (11). At 0.1% emulsifier concentration the surface tension of distilled water at 25°C was reduced considerably from 72.4 dynes/cm to 28.9–36.0 dynes/cm by the emulsifier blends of various carbohydrate polyesters with S-1670 at 50:50 w/w, and blends of individual Ryoto sugar esters. The HLB of the blends and the individual emulsifiers that gave acceptable reduction in surface tension were between 5–16. As expected, the HLB values of the highly lipophilic carbohydrate polyesters were between 2–2.6 and did not result in appreciable reduction of surface tension (generally between 42.0–68.3 dynes/cm) when compared to the hydrophilic emulsifiers, such as S-970 and S-1670, and the blended emulsifiers. Also, the polyester S-170 did not reduce surface tension beyond 70.2 dynes/cm. Alphadim 90AB (90% monoglyceride) showed the greatest reduction in surface tension from 72.4 to 27.8 dynes/cm. Surprisingly, blending of raffinose polystearate with S-1670 reduced the surface tension-synergistically to 33.5 dynes/cm when compared to raffinose polystearate (68.3 dynes/cm) and S-1670 (35.2 dynes/cm) alone. There were also synergistic responses with the other car-

TABLE 1

Surface and Interfacial Tensions of Carbohydrate Polyesters and Commercial Emulsifiers

Emulsifier	Surface tension ^a	Interfacial tension ^b	HLB ^c
	(dynes/cm) @ 0.1%	(dynes/cm) @ 0.05%	
Distilled water/none	72.4	—	—
Xylene + water/none	—	37.6	—
S-170	70.2	N.D. ^d	1
S-570	39.1	9.9	5
S-970	35.5	9.0	9
S-1670	35.2	8.4	16
Alphadim 90AB (90% monoglyceride)	27.8	8.5	N.D.
Sucrose polyoleate	46.6	10.5	3.5
Sorbitol polyoleate	43.8	9.1	2.0
Trehalose polyoleate	42.8	25.1	3.5
Raffinose polystearate	68.3	9.6	N.D.
Raffinose polyester of saff. oil	42.0	N.D.	4.6
Sucrose polyoleate + S-1670 ^e	30.4	7.9	9.8
Sorbitol polyoleate + S-1670	28.9	4.5	9.0
Trehalose polyoleate + S-1670	28.9	8.2	9.8
Raffinose polyester of saff. oil + S-1670	31.6	N.D.	10.3
Raffinose polystearate + S-1670	33.5	8.4	N.D.
S-970 + S-170	36.0	N.D.	5
S-1670 + S-170	32.6	N.D.	8.5

^aSurface tension at room temperature (25°C).

^bInterfacial tension between xylene and water at room temperature.

^cHLB, hydrophile-lipophile balance. The HLB of emulsifier blends were calculated as the weighted average of individual HLB numbers (11). For example, the HLB of trehalose polyoleate + S-1670 blend will be $(3.5 \times 0.50) + (16 \times 0.50) = 9.8$.

^dN.D., not determined.

^eAll emulsifier blends were at 50:50 (w/w).

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bohydrate polyester + S-1670 blends, and with the S-970 + S-170 and S-1670 + S-170 blends. S-170 is approximately 100% polystearate. The unsaturated fatty acids in the carbohydrate polyesters and hydrophilic carbohydrate backbone may have contributed to the observed reduction in surface tension. Interfacial tension between xylene and water was measured at 25°C with 0.05% w/w emulsifier. With the exception of trehalose polyoleate, which gave an anomalous value (25.1 dynes/cm), all the emulsifiers and carbohydrate polyester/emulsifier blends reduced interfacial tension of xylene/water mixtures.

Figure 1 illustrates the effect of selected carbohydrate polyesters concentrations and their blends with S-1670 on surface tension reduction. S-1670 alone reduced surface tension by 52% at 0.5% emulsifier concentration. Individually, trehalose and sorbitol polyoleate did not reduce surface tension appreciably when compared to their blends with S-1670, which resulted in 60% reduction in surface tension at 0.5% concentration. In Figure 1 the data for trehalose polyoleate + S-1670 and sorbitol polyoleate + S-1670 merged and surface tension were reduced to the same extent. Notably, blending of lipophilic carbohydrate polyesters with hydrophilic S-1670 resulted in a synergistic reduction in surface tension as compared to individual emulsifiers.

Figure 2 illustrates the effect of emulsifier concentration on interfacial tension reduction. Trehalose polyoleate alone did not reduce interfacial tension appreciably. Sorbitol polyoleate reduced interfacial tension to 9.1 dynes/cm at 0.05% concentration and above. There was not much added benefit of increasing the emulsifier concentration beyond 0.05% w/w. The hydrophilic emulsifier S-1670 was able to reduce interfacial tension to 5.5 dynes/cm. Interestingly, the trehalose and sorbitol polyoleate blends

with S-1670 resulted in synergistic reduction of interfacial tensions to 4.2 and 4.6 dynes/cm, representing 89% and 88% reduction, respectively. Obviously, the emulsifier blends were better emulsifiers than individual emulsifiers. For a significant surface activity, a proper balance between lipophilic and hydrophilic character in the surfactant is essential (11). A desirable emulsifier must be able to reduce surface or interfacial tension.

Emulsion stability. Most food emulsions will require an emulsifier to prevent coalescence, flocculation and creaming. O/w and w/o food emulsions were prepared with vegetable oil and water with and without emulsifier. Emulsifiers were used at 0.5% concentrations. Emulsion stability was measured over time at room temperature for o/w emulsions and at refrigeration temperature for w/o emulsions. Figure 3 illustrates o/w emulsion separation as a function of time. In the absence of an emulsifier, there was almost an instantaneous separation of the aqueous and oil phases. Trehalose polyoleate was not a good stabilizer of o/w emulsion, probably because of its lipophilic nature. Ryoto sugar ester S-1670 is a hydrophilic emulsifier, and it resulted in close to 54% stability (46% separation). Trehalose polyoleate + S-1670 and S-170 + S-1670 blended emulsifiers were excellent emulsifiers for o/w emulsion, resulting in only 30% separation (70% stability). Figure 4 illustrates the effect of emulsifiers on the stability of w/o emulsions at refrigeration temperature. As expected, the lipophilic emulsifier trehalose polyoleate (HLB 3.5) was an excellent w/o emulsion stabilizer, allowing only 7% separation in 2 hr, and 10% separation over 48 hr. The sugar ester S-170 (HLB 1) allowed 6% separation in 8 hr, but the separation increased to 50% over 48 hr. However, the S-170+S-1670 50:50 w/w blend was an excellent stabilizer of w/o emulsion with only 6% separa-

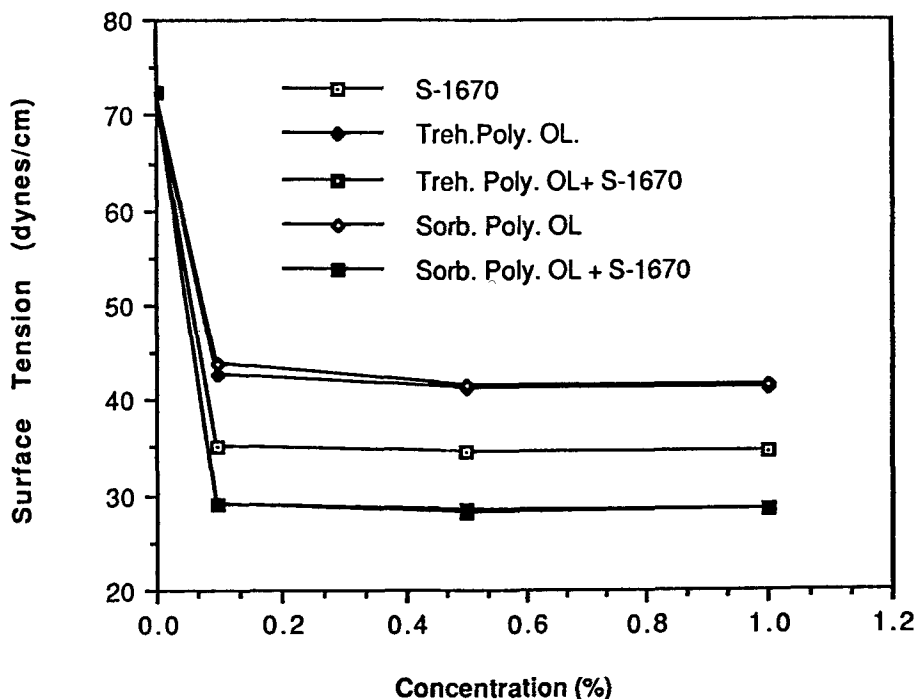


FIG. 1. Effect of concentrations for selected carbohydrate polyesters and their blends on surface tension reduction. Surface tension was measured at room temperature (see experimental section for details). Treh.Poly.OL, trehalose polyoleate; S-1670, Ryoto sugar ester (75% monostearate); and Sorb. Poly. OL, sorbitol polyoleate.

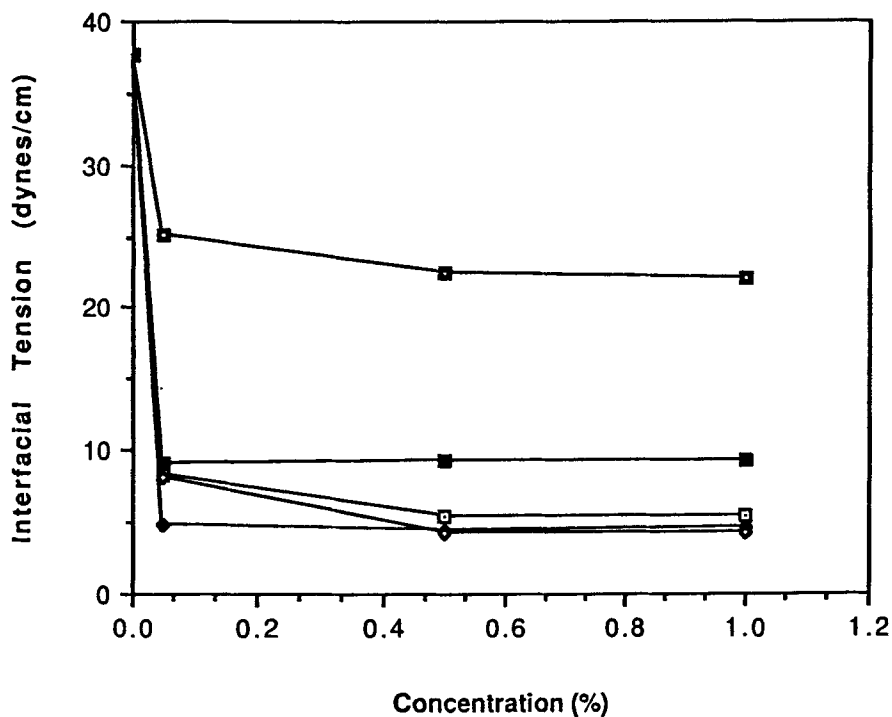


FIG. 2. Effect of emulsifier concentration on interfacial tension reduction. Interfacial tension was measured at 25°C. See Figure 1 for legends.

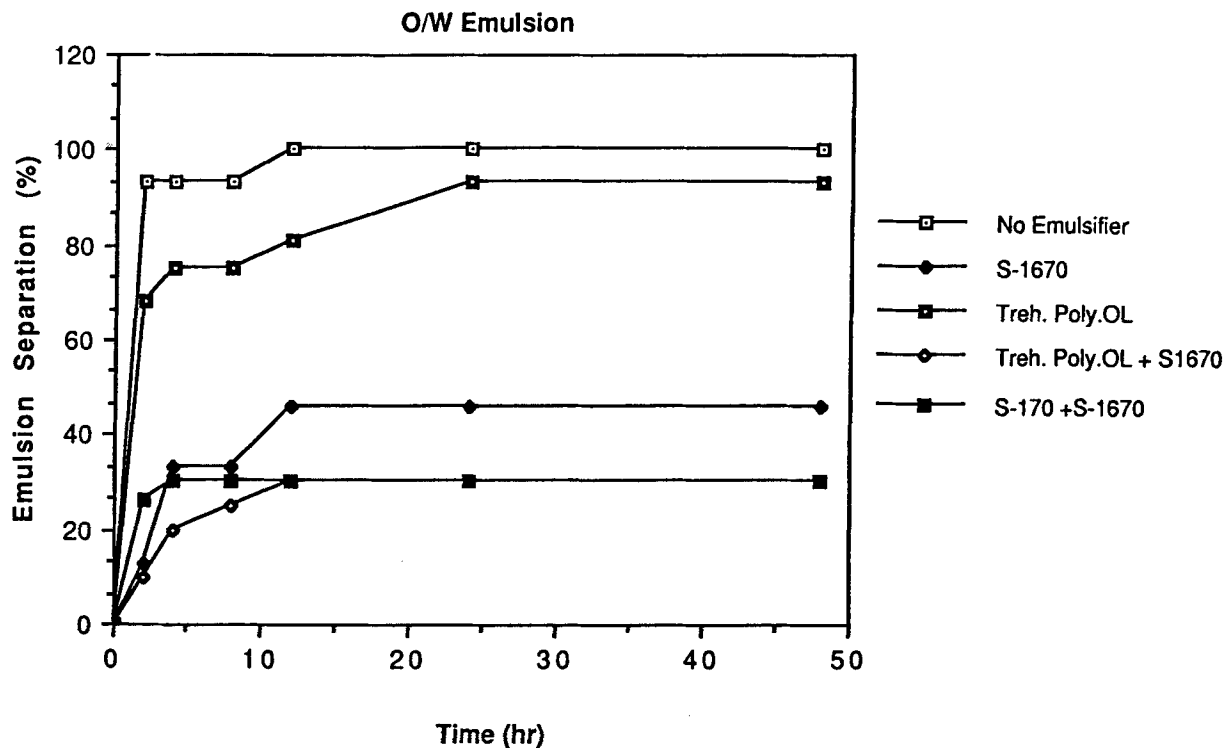


FIG. 3. Stability of o/w emulsions as a function of time at room temperature. Control contained no emulsifier. A 0.5% emulsifier concentration was used. S-170, Ryoto sugar ester (100% polystearate).

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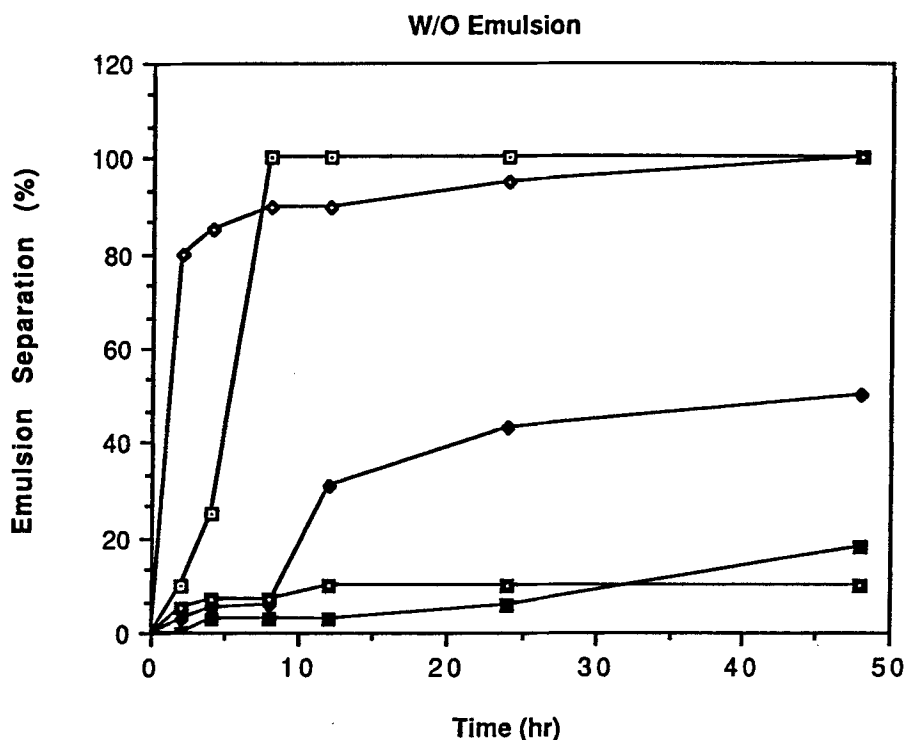


FIG. 4. Effect of emulsifier on the stability of w/o emulsions at refrigeration temperature. A 0.5% emulsifier concentration was used. Control contained no emulsifier. See Figure 3 for legends.

tion in 24 hr. Sorbitol polyoleate was comparable to trehalose polyoleate in stabilizing w/o emulsion (data not shown). Surprisingly, a blend of trehalose polyoleate + S-1670 did not result in a stable w/o emulsion. In fact, 90% separation of the phases was observed after 8 hr storage at refrigeration temperature. The reasons for this phenomenon are not clear at this time and require further investigation. In the absence of an emulsifier, there was 100% separation of the phases. Blending of lipophilic carbohydrate polyesters with hydrophilic emulsifiers produced stable o/w emulsions but no stable w/o emulsions. However, the carbohydrate polyesters, when used alone, were excellent w/o emulsion stabilizers. This is consistent with their low HLB values (2.0-4.6), as previously suggested (9,10).

The results of this investigation suggest that carbohydrate polyesters are usable as emulsifiers for o/w and w/o emulsions. Depending on the physical properties of the finished product, the correct emulsifier or emulsifier blends can only be selected by experimentation.

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REFERENCES

1. Haumann, B.F., *J. Am. Oil Chem. Soc.* 63:278 (1986).
2. LaBarge, R.G., *Food Technol.* 42:84 (1988).
3. Breyer, L.M., and C.E. Walker, *J. Food Sci.* 48:955 (1983).
4. Ebeler, S.E., and C.E. Walker, *Cereal Chem.* 60:270 (1983).
5. Watson, K.S., and C.E. Walker, *Ibid.* 63:62 (1986).
6. Chung, H., P.A. Seib, K.F. Finney and C.D. Magoffin, *Ibid.* 58:164 (1981).
7. Pomeranz, Y., *Ibid.* 58:190 (1981).
8. Akoh, C.C., and B.G. Swanson, *J. Food Sci.* 52:1570 (1987).
9. Akoh, C.C., and B.G. Swanson, *J. Am. Oil Chem. Soc.* 66:1581 (1989).
10. Akoh, C.C., and B.B. Swanson, *J. Food Sci.* 55:236 (1990).
11. Rosen, M.J., *Surfactants and Interfacial Phenomena*, John Wiley and Sons, New York, 1989, pp. 207-336.
12. Meyer, R.S., C.C. Akoh, B.G. Swanson, D.B. Winter, J.M. Root and M.L. Campbell, U.S. Patent no. 4,973,489 (1990).
13. Alexander, A.E., and J.B. Hayter, in *Physical Methods of Chemistry*, John Wiley and Sons, New York, 1971, pp. 501-555.
14. *Ryoto Sugar Ester Technical Information*, Mitsubishi-Kasei Food Corporation, Tokyo, 1987, pp. 1-20.

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