Emulsification Properties of Polyesters and Sucrose Ester Blends II: Alkyl Glycoside Polyesters

Casimir C. Akoh* and **Chigozie V. Nwosu**
Department of Food Science and Animal Industries, School of Agriculture and Home Economics, Alabama A&M University, Huntsville, AL 35762

Surface active properties such as surface and interfacial tension reductions and stability of oil-in-water (o/w) and water-in-oil (w/o) emulsions by alkyl glycoside fatty acid polyesters, a potential fat substitute, and emulsifier blends of alkyl glycoside polyesters and Ryoto sugar esters were investigated.

Our results indicate that blending of lipophilic and hydrophilic emulsifying agents produces a synergistic effect on reduction of surface and interfacial tensions and may, in some cases, result in more stable emulsions. Alkyl glycoside polyesters may be suitable for w/o emulsions, such as margarine and butter, and their blends with hydrophilic emulsifiers will produce reduced calorie emulsifiers suitable for use in o/w emulsions, such as salad dressing. There appears to be great potential for using such emulsifier blends in food, cosmetics and pharmaceutical applications.

KEY WORDS: Alkyl glycosides, emulsifiers, methyl glucoside polyesters, surface active properties.

Alkyl glycoside fatty acid esters (mono- and diesters) are excellent digestible oil-in-water (o/w) emulsifiers (1,2). Ryoto sugar esters (S-570 to S-1670) are FDA-approved nonionic emulsifiers suitable for food, cosmetic and pharmaceutical applications. Alkyl glycoside fatty acid polyesters (tri- and tetraesters) are potential nondigestible fat substitutes with functional and physical properties resembling conventional triglycerides (3). Alkyl glycoside polyesters are not fully hydrolyzed by intestinal lipases, due to steric hindrance, and consequently are poorly absorbed (3,4).

The hydrophile-lipophile balance (HLB) of alkyl glycoside polyesters (HLB 3.2–3.4) resembles the HLB value of sucrose polyoleate (HLB 3.5), indicating potential use as a water-in-oil (w/o) emulsifier (3). The HLB values are indicators of behavioral characteristics and do not indicate emulsifying efficiency. The selection of a suitable emulsifier for an o/w or a w/o emulsion must be determined by experimentation. However, a low HLB value (such as 3–6) will promote or stabilize w/o emulsions, an intermediate value (*e.g.*, 8–13) will stabilize o/w emulsions, and a high value (such as 15–18) will act as a solubilizer (5,6). Oil-in-water emulsions can be prepared with certain surfactants over the entire range of HLB numbers from 2–17 (7). Emulsifying agents that are preferentially lipophilic (oil-soluble) form w/o emulsions, and a mixture of a preferentially lipophilic surface-active agent and a preferentially hydrophilic (water-soluble) one often produces better and more stable emulsions than an individual surfactant (7).

Alkyl glycoside and sucrose esters of widely different HLB values can be prepared by varying: i) the alkyl chainlength of the ester group; ii) the degree of unsaturation of the ester group; iii) the number of ester groups per molecule; iv) the chainlength of the alkyl group; or v) by blending emulsifiers of different HLB values. In general, for a surfactant to act as an emulsifier, it must show good surface activity and produce a low interfacial tension in the particular system in which it is to be used. This means that it must have a tendency to migrate to the interface, rather than to remain dissolved in either one of the bulk phases. It must form, at the interface (either by itself or with other adsorbed molecules) an interfacial film that is condensed, because of lateral interactions between the molecules comprising the interfacial film. Finally, it must migrate to the interface at such a rate that the interfacial tension is reduced to a low value in the time during which the emulsion is being produced (7). The possibility of preparing emulsifier blends capable of stabilizing either o/w and/or w/o emulsions for possible food, cosmetics and pharmaceutical applications has not received adequate attention. Indeed, few reports have been published on the surface activity of alkyl glycoside polyesters and blends thereof with commercial emulsifiers.

The objectives of the present investigation were to evaluate the potential of alkyl glycoside polyesters, a potential fat substitute, and blends of alkyl glycoside polyesters with commercial emulsifiers and Ryoto sugar esters to: i) reduce surface tension; ii) reduce interfacial tension; iii) stabilize o/w and w/o emulsions; and iv) study the synergistic effects of blending alkyl glycoside polyesters with other emulsifiers.

MATERIALS AND METHODS

Synthesis of alkyl glycoside polyesters. Synthesis of pure methyl glucoside polyoleate and octyl glucoside polyester of peanut oil was based on procedures described previously (3).

Measurement of surface and interfacial tension. Surface tension in distilled water and interfacial tension between water an xylene at 25°C were measured with a CSC-DuNouy Interfacial Tensiometer Model 70545 (CSC Scientific Company, Fairfax, VA) (8) as described in the preceding paper (9).

HLB determination. The determination of HLB values of alkyl glycoside polyesters has been described (3,10). The HLB values of blended emulsifiers was calculated as the weighted average of the individual HLB numbers (7). In all blends the ratio was 1:1 (w/w). For example, if a mixture of 50% S-1670 (HLB 16) and 50% S-170 (HLB 1) is to be used, then the HLB of the emulsifier blend (S-1670 + S-170) should be (16 × 0.05) + (1 × 0.50) = 8.5.

Measurement of food emulsion stability. The stability of o/w and w/o emulsions were measured as previously described (9).

RESULTS AND DISCUSSION

Table 1 shows the properties of selected commercial emulsifiers and alkyl glycoside fatty acid polyesters used in this study. The low HLB value of Ryoto S-170

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*To whom correspondence should be addressed at Dept. of Food Science and Animal Industries, Alabama A&M University, P.O. Box 264, Huntsville, AL 35762.

TABLE 1

Properties of Selected Commercial Emulsifiers and Alkyl Glycoside Polyesters

Emulsifier	Approximate HLB[a]	Approximate % monoester	Approximate % di-, tri- or polyester
Ryoto S-170[b]	1	0	100
S-570	5	30	70
S-970	9	50	50
S-1670	16	75	25
Alphadim 90AB	ND[c]	90	10
Octyl Glu-Poly peanut oil	3.2	0	100
MGP-OL[d]	3.4	0	100

[a] Hydrophile-lopophile balance values.

[b] From 1987 Ryoto Sugar ester technical information (14).

[c] ND, not determined.

[d] Methyl glucoside polyoleate.

TABLE 2

Effect of Emulsifier Concentration on Surface Tension[a]

	Surface tension (dynes/cm) Concentration %			
Emulsifier	0.1	0.5	1.0	HLB
S-170	70.2	—	—	1
S-570	39.1	38.9	38.9	5
S-970	35.5	34.1	34.1	9
S-1670	35.2	34.5	34.4	16
MGP-OL	41.9	38.9	38.9	3.4
Alphadim 90AB (90% monoglyceride)	27.8	28.9	28.9	ND
Octyl Glu-Poly peanut oil	42.2	42.0	42.0	3.2
S-970 + S-170, 1:1 (w/w)	36.0	35.4	35.3	5.0
S-1670 + S-170, 1:1 (w/w)	32.6	33.5	33.5	8.5
MGP-OL + S-1670, 1:1 (w/w)	29.9	29.4	29.3	9.7
Octyl Glu-Poly peanut oil + S-1670 1:1 (w/w)	29.4	28.9	28.9	9.6
Alphadim 90AB + MGP-OL, 1:1 (w/w)	26.6	26.6	26.5	ND
Distilled water (control)	72.2	—	—	—

[a] Legends as in Table 1.

(HLB 1) suggests a w/o emulsifier, while the high HLB of 16 for S-1670 suggests an o/w emulsifier. The HLB values of alkyl glycoside polyesters (HLB 3.2–3.4) suggest that values are algebraically additive and that a blend of emulsifiers (MGP and Ryoto sugar esters) needed to produce maximum o/w or w/o emulsion stability could be obtained by experimentation. Gupta *et al.* (6) obtained an HLB range of 4–16 by blending sucrose esters and mixed glycerides to produce good o/w emulsifiers. The alkyl glycoside polyester and S-170 were highly substituted and, therefore, more lipophilic than the less substituted hydrophilic S-570, S-970, S-1670 and Alphadim 90AB.

Surface and interfacial tension. Table 2 illustrates the effect of emulsifier concentration and HLB on surface tension of various sugar esters, alkyl glycoside polyester and blends thereof compared to distilled water as control. At emulsifier concentration between 0.1 and 0.5%, the surface tension of water at 25°C was reduced considerably, from 72 dynes/cm to 26.6, 28.9, and 29.4 dynes/cm by 1:1 (w/w) blends of Alphadim 90AB + MGP-OL, octyl glucoside polyoleate + S-1670, and MGP-OL + S-1670, respectively. Ryoto S-170 at 0.1% concentration did not reduce the surface tension of water, possibly because S-170 is highly lipophilic. However, S-970, S-1670 and a 1:1 (w/w) blend of S-1670 + S-170 were excellent emulsifiers and reduced surface tension of water to 34.1, 34.5 and 33.5 dynes/cm, respectively. Clearly, the alkyl glycoside polyesters alone did not reduce surface tension as much as did blends of alkyl glycoside polyesters with Ryoto esters and Alphadim 90AB. Alphadim 90AB is a commercially distilled o/w emulsifier containing 90% monoglyceride of mixed fatty acids. The monoglyceride alone seemed to be the best in reducing surface tension among the individual emulsifiers tested. Figure 1 further illustrates the synergistic effect of blending MGP-OL with S-1670 (lipophilic and hydrophilic emulsifiers, respectively). Surface tension was synergistically reduced by the emulsifier blend compared to either of the emulsifiers alone. Emulsifiers with low HLB (of 1–3.4) did not reduce surface tension as much as emulsifiers of HLB 5–16. Thus, HLB values only indicated behavioral characteristics, and suitable emulsifiers were determined by experiment.

Table 3 illustrates percent reduction of interfacial tension between xylene and water at 0.05% emulsifier concentration. Octyl glucoside polyester of peanut oil + S-1670 [1:1 (w/w) blend] reduced the interfacial tension of

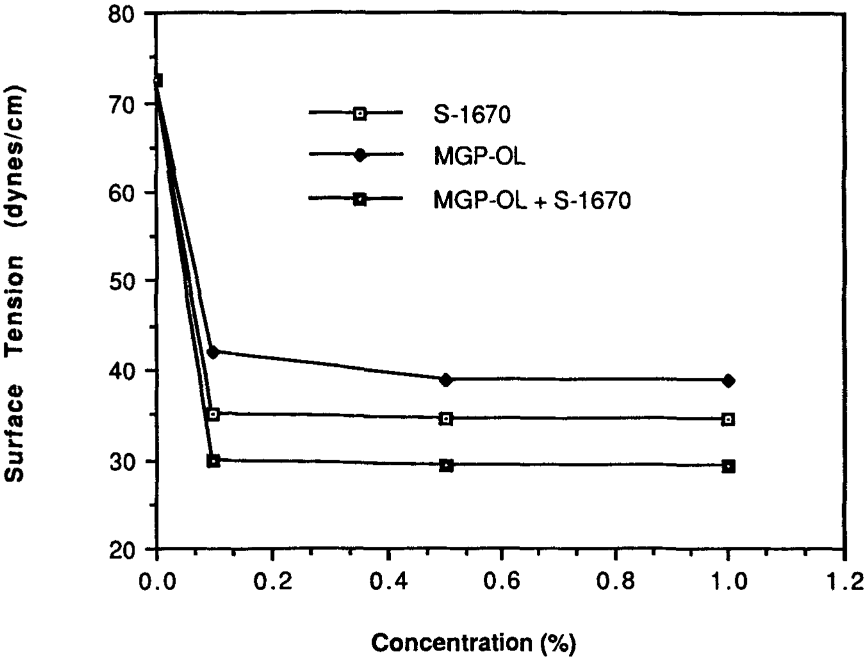

FIG. 1. Reduction of surface tension of water control (72.4 dynes/cm) compared to methyl glucoside polyoleate, S-1670, and blended emulsifier as a function of concentration. Surface tension was measured at 25°C as described in the Experimental Section. MGP-OL, methyl glucoside polyoleate; and S-1670, Ryoto sugar ester (approximately 75% monostearate).

TABLE 3

Percent Reduction of Interfacial Tension Between Xylene and Water at 0.05% Emulsifier Concentration[a]

Sample	Interfacial tension (dynes/cm)	% Reduction
Xylene + water (control)	37.6	0
S-570	9.9	73.7
S-1670	8.4	77.7
MGP-OL	18.9	49.7
Alphadim 90AB (90% monoglyceride)	8.5	77.4
Octy Glu-Poly peanut oil	7.9	79.0
MGP-OL + S-1670, 1:1 (w/w)	8.7	76.7
Octyl Glu-Poly peanut oil + S-1670, 1:1 (w/w)	5.0	86.7
Alphadim 90AB + MGP-OL 1:1 (w/w)	8.5	77.4

[a] Legends as in Table 1.

xylene/water mixture (control) by 86.7%, whereas MGP-OL only reduced interfacial tension by 49.7%. The results indicated that S-570, S-1670 and emulsifier blends were better emulsifiers for o/w emulsions than MGP-OL. Figure 2 compared the ability of S-1670, MGP-OL and their blends to reduce interfacial tension of o/w emulsions. Clearly, MGP-OL + S-1670 synergistically reduced the interfacial tension from about 37.6 dynes/cm to 4.5 dynes/cm at 0.5% concentration. MGP-OL alone reduced interfacial tension to 18.4 dynes/cm at the same concentration. It has been suggested (7) that emulsifying agents that are preferentially oil-soluble form w/o emulsions and a mixture of preferentially oil-soluble surface-active agents, and a preferentially water-soluble one often produces better and more stable emulsions than an individual surfactant. The properties required of a range of emulsifiers designed for food use, cosmetics and pharmaceuticals include an HLB range of 2–17, low toxicity and irritancy and stability to hydrolysis (6,11). One of the most important characteristics of a surfactant is its ability to reduce surface and interfacial tensions. Surface and interfacial tensions measured by the DuNouy ring method (8)

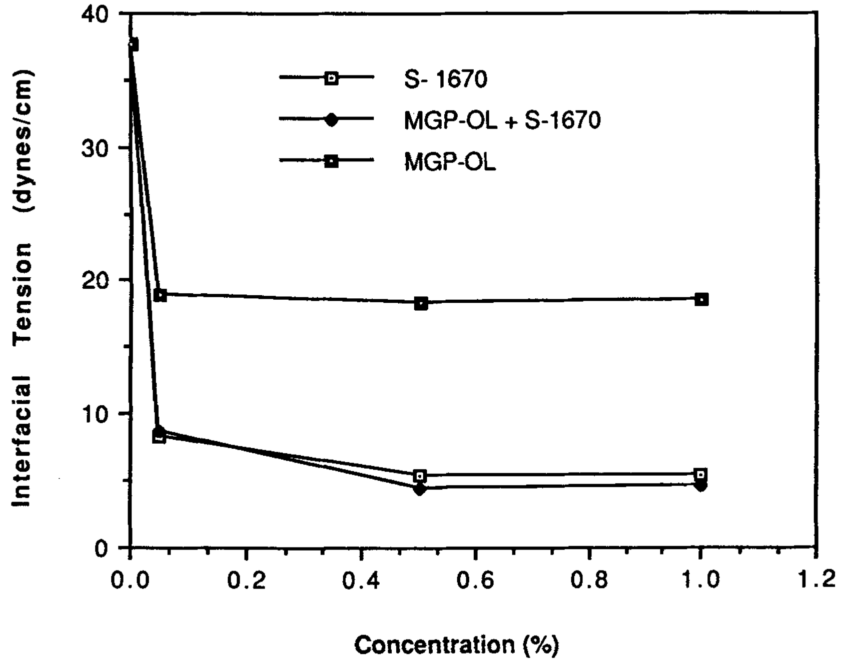

FIG. 2. Reduction of interfacial tension between xylene and water by methyl glucoside polyoleate, S-1670, and blended emulsifier as a function of concentration. Conditions were as described in the Experimental Section. Interfacial tension was measured at 25°C. See Figure 1 for legends.

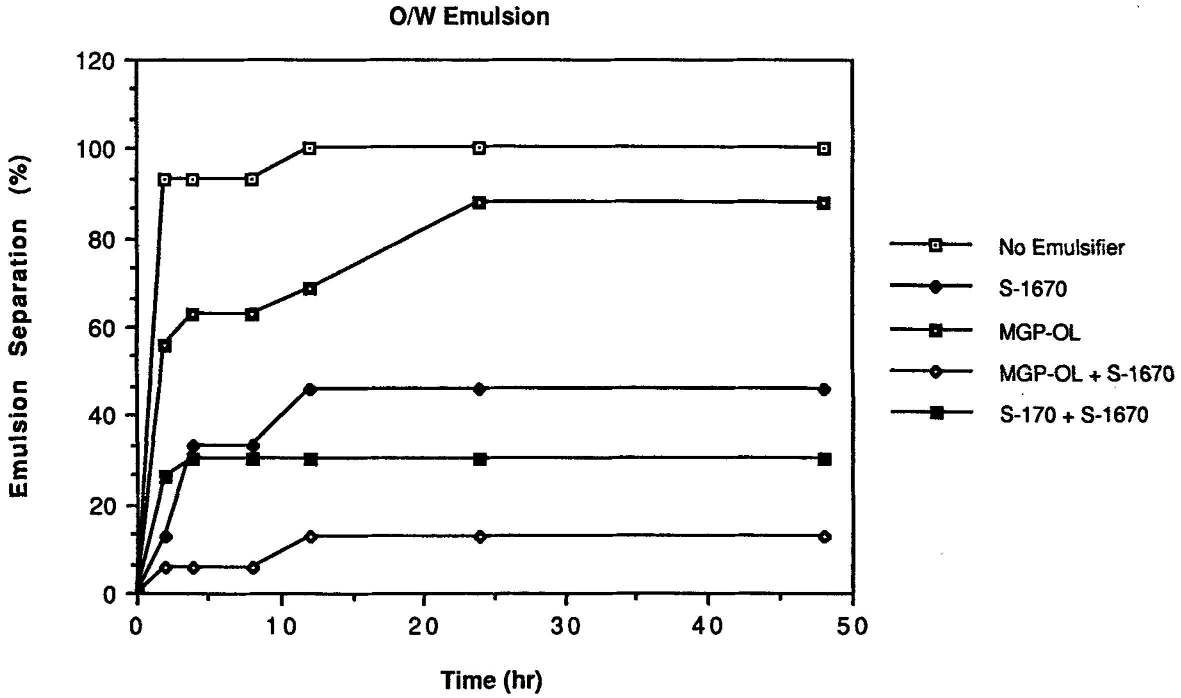

FIG. 3. Stabilization of o/w emulsions (vegetable oil/water) by methyl glucoside polyoleate (MGP-OL), S-1670, and emulsifier blends at room temperature. A 0.5% emulsifier concentration was used. Control consisted of vegetable oil + water without an emulsifier.

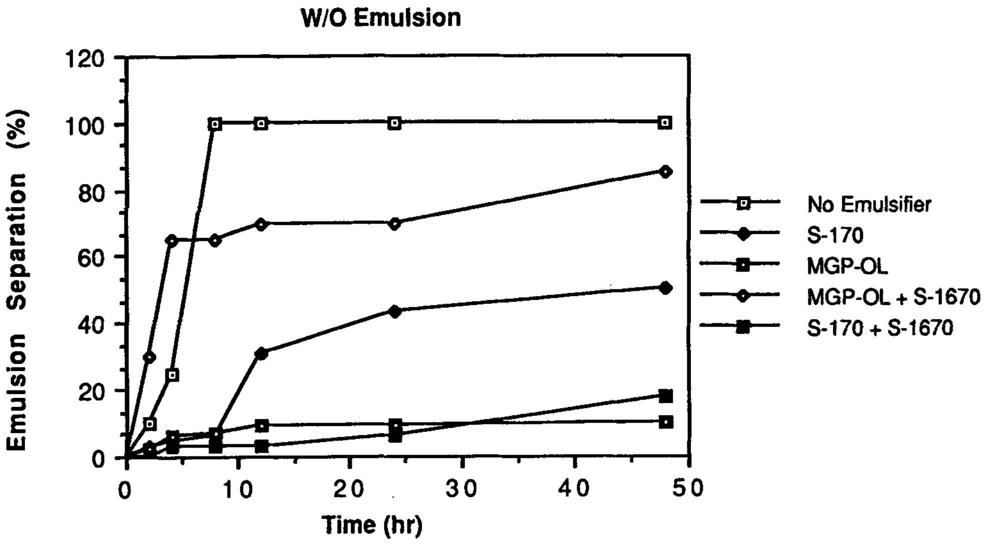

FIG. 4. Stabilization of w/o emulsions by methyl glucoside polyoleate, S-1670, and emulsifier blends at refrigeration temperature. A 0.5% emulsifier concentration was used. Control consisted of oil + water and no emulsifier.

were greatly reduced by S-1670 and MGP-OL + S-1670 blend.

Emulsion stability tests. Ability to stabilize emulsions is another classical test for a surfactant (12). Food emulsions were prepared from water and vegetable oil with and without an emulsifier. Emulsion stability was measured at room temperature for o/w emulsions and at refrigeration temperature for w/o emulsions. A 0.5% emulsifier concentration was used in both cases. The emulsions were allowed to separate, and percent separation was calculated as a function of time. Within 2 hr, the water and vegetable oil layers in o/w emulsion were completely separated in the absence of an emulsifier (Fig. 3). The MGP-OL was not a good stabilizer for o/w emulsion. However, a 1:1 (w/w) blend of MGP-OL + S-1670 exhibited the best emulsion stability at room temperature for up to 48 hr (less than 13% separation). The stability impacted by the emulsifier blends was synergistic. Also, the S-170 + S-1670 1:1 (w/w) blend showed a marked stabilizing ability (less than 30% separation) of o/w emulsions. The hydrophilic emulsifier S-1670 alone showed intermediate stabilizing ability (46% separation). The trend was somewhat different for w/o emulsions (Fig. 4). In the presence of 0.5% MGP-OL, the stability of w/o emulsion was greatly enhanced (less than 10% separation) while the MGP-OL + S-1670 blend showed significantly reduced ability to stabilize w/o emulsion. The S-170, which is a lipophilic emulsifier, showed intermediate stabilizing ability (50% separation) when compared to the lipophilic MGP-OL. The methoxy (CH_3O-) group at the C-1 anomeric carbon of methyl glucoside and the oleate may have some influence on the unique ability of the alkyl glycoside polyesters to stabilize w/o emulsions. Previous reports (13) have shown that stabilities of various lactitol fatty acid esters and propoxylated lactitol esters were affected primarily by the fatty acid constituent of the ester. The palmitates produced emulsions with better stability than the stearates, and the palmitate/stearates mixtures gave emulsions of intermediate stability. In the present study unsaturation in the ester group and the chainlength of the alkyl group may have contributed more to the enhanced stability of w/o emulsions by MGP-OL. Notably, the S-170 + S-1670 blend (calculated HLB 8.5) was good in stabilizing o/w and w/o emulsions.

The results of this investigation clearly suggest that blending of emulsifiers and selection of emulsifiers for particular applications by experimentation is a more attractive alternative to using individual emulsifiers and selecting emulsifiers based on HLB values. By blending and experimenting, emulsifier types and concentrations can be selected that are required to stabilize o/w and w/o emulsions and to reduce surface and interfacial tensions for food, pharmaceutical and cosmetics applications. Obviously, the use of alkyl glycoside polyesters as emulsifiers in o/w and w/o emulsions is an attractive possibility for making reduced-calorie emulsions in salad dressing, butter, margarine, low fat spreads and shortenings.

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