Partially Saponified Triglyceride Ethoxylates[1]

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ABSTRACT: Various triglycerides (coconut oil, palm kernel oil, tallow) were ethoxylated with a proprietary catalyst (calcium/aluminum alkoxide complex partially neutralized in an alcohol ethoxylate base) to obtain triglyceride ethoxylates. Triglyceride ethoxylates were then partially saponified with sodium hydroxide to form mixtures of mono-, di-, and triglyceride ethoxylates, fatty acid soap, and glycerol ethoxylate. These mixtures were characterized in terms of physical properties, surface activity, and mildness. Partially saponified triglyceride ethoxylates were found to be unexpectedly mild and capable of imparting mildness to other surfactants.

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KEY WORDS: Ethoxylation, fatty acid ethoxylates, glyceride ethoxylates, saponification, soap, triglyceride ethoxylates.

Ethoxylation is the most common method for adding a nonionic hydrophile to an organic hydrophobe. Prior to 1989, substrates suitable for ethoxylation were thought to require a labile hydrogen, most commonly a hydroxyl hydrogen, in order for ethoxylation to occur. In the late 1980s, the concept of ethoxylating esters was introduced by Hoechst and Henkel (1,2). Hoechst demonstrated that ethoxylation of esters was feasible using catalysts based on alkali and alkali earth metals (e.g., sodium hydroxide, sodium methoxide, barium hydroxide, etc.), while Henkel showed that calcined hydrotalcite (aluminum/magnesium oxide complexes) had potential as well. Relatively poor reactivities and conversions, however, prevented these catalysts from being utilized commercially.

In the early 1990s, Vista Chemical Company (now CONDEA Vista Company, Houston, TX) developed a commercially viable process for ethoxylating esters (3). Their process utilized a more complex alkoxylation catalyst (activated calcium and aluminum alkoxides) that efficiently and effectively inserted ethylene oxide between the carbonyl carbon and the ester oxygen. Immediately thereafter, Lion Corporation (Tokyo, Japan) demonstrated that a magnesium/aluminum oxide-based catalyst also worked well (4). Since then, the development and use of ester alkoxylates have become an active area of research (5–22).

This paper deals with an extension of ester alkoxylation technology. Previous studies have demonstrated that the CONDEA Vista catalyst (a calcium and aluminum alkoxide complex partially neutralized in an alcohol ethoxylate base) can be used to ethoxylate esters, including triglycerides (5,13–16). It is also known that mono- and diglyceride ethoxylates are mild surfactants (23). The object of this research was first to prepare triglyceride ethoxylates and then partially saponify them to obtain a mild surfactant blend of mono-, di-, and triglyceride ethoxylates and fatty acid soap. It was thought that such a blend would make a lower-cost surfactant for mild personal-wash bars, pastes, and gels.

This paper details our initial studies on partially saponified triglyceride ethoxylates (PSTE). It describes the preparation and cursory assessment of PSTE made from three different triglycerides. The impacts of surfactant structure (carbon chain length, unsaturation, degree of ethoxylation, degree of saponification, type of counter-cation) as well as end-use applications have yet to be examined.

EXPERIMENTAL PROCEDURES

Ethoxylation. Ethoxylations were performed in a conventional 400-mL stainless steel autoclave (fabricated in-house) equipped with a magnetic stirring bar, an internal cooling line, and a thermocouple to monitor reaction temperature. The reactor (autoclave) was contained in an insulated heating block. Temperature was monitored and heat controlled by an I^2R (Cheltenham, PA) Therm-O-Watch model TCP3-1200 temperature controller. Compressed air was used for cooling and was controlled by an I^2R Therm-O-Watch model L9-1500 RTD controller. A 500-mL bomb containing ethylene oxide (EO) under 50 pounds of N_2 pressure was connected in parallel with a graduated siteglass and connected to the autoclave *via* stainless steel tubing.

The experimental procedure consisted of the following steps: (i) charging the EO reservoir, (ii) charging the reactor with feedstock (to produce a 300-g batch), (iii) heating the reactor to 175°C, (iv) nitrogen stripping the reactor for 15 min to remove moisture, (v) the addition of 3.5 g of ethoxylation catalyst, (vi) 5 min nitrogen stripping to further remove moisture, (vii) EO addition to the feedstock, (viii) reaction of the EO until a constant pressure is

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reached, (ix) cooling the reactor to 70–80°C while flushing with nitrogen and with removal of product at 70–80°C while still a liquid.

Ethoxylation catalyst. Ethoxylations were performed with a proprietary alkoxylation catalyst complex (called NOVEL® II; CONDEA Vista Company, Houston, TX) consisting of a calcium and aluminum complex partially neutralized in an alcohol ethoxylate base (24). This Ca/Al alkoxide catalyst was shown to be an effective alkoxylation catalyst for producing "peaked" or "narrow-range" alcohol ethoxylates and for the alkoxylation of various esters (3, 5, 14–16, 25).

Saponification. Saponifications were performed in a three-necked 500-mL round-bottom flask set in a temperature-controlled oil bath. The flask was equipped with overhead mechanical stirring. Nitrogen was introduced into one-neck of the flask *via* a Pasteur pipette in a rubber stopcock.

The saponification procedure consisted of the following steps: (i) 150 g of ethoxylate was placed in the flask, (ii) the flask/ethoxylate was heated to 95°C with stirring under nitrogen, (iii) the targeted volume of standardized 50% sodium hydroxide (NaOH; Aldrich Chemical Company, Milwaukee, WI) was added dropwise *via* a glass syringe, (iv) 10 min after the addition of the base, temperature was increased to 115°C, (v) 10 min later, temperature was increased to 160°C, (vi) after 60 min, a few drops of distilled water were added to prevent dehydration of the product (to prevent formation of the alkoxide due to the presence of any unreacted NaOH), which is detrimental to product color and yield, (vii) after 2 h, the product was titrated to determine the degree of saponification; if the level of saponification was not achieved, stirring under nitrogen was continued, and (viii) once the level of saponification was obtained, residual base was quenched with addition of an excess (0.5–1%) of myristic acid (99.5+%).

Note: Since these experiments were performed, we have determined that the addition of 5% water to the triglyceride after the caustic addition but prior to saponification significantly reduces the time needed for saponification to occur (from 12–18 h to *ca.* 90 min) and at a lower temperature (less than 100°C). The water was subsequently removed by heating to 160°C under a stream of nitrogen.

Determination of triglyceride molecular weight. Saponification number was used to estimate the molecular weight of triglycerides, based on the assumption that three moles of KOH are consumed during saponification for every mole of triglyceride, such that :

$$\text{triglyceride molecular weight} = 168{,}330/\text{saponification number} \quad [1]$$

Saponification number was determined by potentiometric titration using a Metrohm Model 670 titroprocessor equipped with a Brinkmann (Westbury, NY) combination pH electrode. The general procedure consisted of first adding 0.1 M alcoholic potassium hydroxide (KOH; Aldrich Chemical Company) and next heating and refluxing the sample for 1 h, followed by titration of the residual base with standardized 0.1 N hydrochloric acid (J.T. Baker, Phillipsburg, NJ). The saponification number was determined as the weight (mg) of KOH required to saponify 1 g of the sample.

Determination of fatty acid soap content. Fatty acid (soap) content was determined by potentiometric titration using a Brinkmann model 670 potentiometer.

Determination of ethoxylated glycerol content. Ethoxylated glycerol (formed during saponification) and polyethylene glycol (formed during ethoxylation) are similar in nature, and a method to distinguish them is not yet available. Due to the relatively high degree of saponification, it is assumed that the majority of the ethoxylated glycerol/polyethylene glycol fraction is ethoxylated glycerol.

The ethoxylated glycerol/polyethylene glycol fraction was quantitated using high-performance liquid chromatography (HPLC). The HPLC system consisted of an isocratic pump and refractive index detector both manufactured by Waters (Milford, MA), an Alcott (Norcross, GA) autosampler, C8 and C18 reversed-phase columns followed by a size-exclusion column. This setup is based on a method developed by Winkle (26) and McCormick and Karger (27). The columns [Phase Separation (Norwalk, CT) Spherisorb C_8 250 mm × 4.6 mm; Phase Separation Spherisorb ODS2 250 mm × 4.6 mm; and Waters Ultrahydrogel™ 120 300 mm × 7.8 mm] and detector were maintained at 40°C. The eluant was methanol/water at 80:20 vol/vol. With a flow rate of 0.8 mL/min, the ethoxylated glycerol/polyethylene glycol fraction eluted in *ca.* 15 min. Quantitation was by polyethylene glycol external standards.

Surface properties (Gibbs' plots). Gibbs' plots (surface tension vs. surfactant concentration) were obtained using a Kruss (Hamburg, Germany) Model K12 tensiometer. To buffer ionic strength, all test solutions contained 0.01 molar sodium sulfate.

Flash foaming. The ability to generate flash foam was measured using a Schlag foam generation apparatus. This test method involves visually reading the level of foam produced after perforated disks are plunged through 100-mL solutions of test surfactants. Foam measurements include the total volume of foam plus solution, such that a reading of 110 mL represents a low-foaming surfactant since the initial reading before foam generation was 100 mL (the initial solution volume). The apparatus is described elsewhere (28).

Hardness testing. Hardness was evaluated using a Shore Durometer (Shore Conveloader No. 998; Shore Instrument Co., Jamaica, NY). Test methodology was based on ASTM D-2240.

Melting point. Melting points were determined using a Fisher (Pittsburgh, PA) melting point apparatus.

Mildness testing. Mildness was measured using two methodologies: Microtox™ testing and human patch tests.

Mictrotox testing. Microtox™ is a bacterial toxicity test that has been used to predict skin sensitivity response (harshness) (29,30). The method, prescribed by Azur Environmental, Inc. (Carlsbad, CA), utilizes the luminescence response of the test organism *Vibrio fischeri*. Toxicity is expressed as EC_{50} which is the calculated concentration of test substance that yields 50% of the light response observed in the control.

Human patch test. Tests were performed by Stephen and Associates, Inc. (Carrollton, TX) to estimate the mean number of days of continuous exposure that would produce a threshold reaction (clinical grade of "3" showing erythema and papules) and to estimate a cumulative irritation score. Aliquots of 1% (wt/vol) of test samples were applied to patches placed onto the backs of 14 human test subjects for a total of 7 d using a modification of the procedures of Lanman *et al.* (31). Sodium lauryl sulfate was used as a positive control. The scoring and interpretation of the skin responses were according to Berger and Bowman (32), whereby the combinations of numerical and letter grading of skin responses are converted to a single numerical score. This single numerical score is then interpreted as "mild" (no experimental irritation), "probably mild" (evidence of slight potential for very mild irritation under test conditions), "possibly mild" (evidence of moderate potential for mild cumulative irritation under test conditions), "experimental cumulative irritant" (evidence of strong potential for mild-to-moderate cumulative irritation under test conditions), "experimental primary irritant" (evidence of potential for primary irritation under conditions of test).

Triglycerides used in study. Three triglycerides were used in this study. Compositional information for each triglyceride is given in Table 1.

Reference standards used in study. Four reference standards were used in the study, as follows:

- Sodium cocoyl isethionate—Tauranol I-78 Flakes, from Finetex (Elmwood Park, NJ)
- Dove® bar soap—Lever Brothers Company (New York, NY), acyl isethionate-based mild bar soap
- Ivory® bar soap—Procter & Gamble Co. (Cincinnati, OH), fatty acid-based bar soap
- Sodium dodecyl (lauryl) alcohol sulfate, 98%—Aldrich Chemical Company

These were chosen because initial studies suggested that PSTE might have application in personal-wash bars because they were solid, appeared to lather well, and were thought to be mild.

RESULTS AND DISCUSSION

Preparation of partially saponified triglyceride ethoxylates. PSTE were prepared using the process described in Figure 1. Each triglyceride was ethoxylated to 60 or 70% EO. This range of ethoxylation was chosen as a reasonable compromise between a high level of EO to make the mono-, di-, and triglycerides water-soluble, and a lower level of EO to maximize surface properties. The resultant triglyceride ethoxylate (TG ETO) was then partially-saponified to form a mixture of mono-, di-, and TG ETO plus ethoxylated glycerol and fatty acid soap. For these initial studies, we targeted slightly more than 50% saponification to break slightly more than half of the ester linkages and to obtain high concentrations of the mono- and diglyceride ethoxylates. We predicted these species would be the mildest, while keeping the glycerol ethoxylate level reasonably low. Three triglyceride feedstocks (coconut oil, tallow, and palm kernel oil) were ethoxylated and partially saponified, as described in Table 2.

Composition of PSTEs. The composition of the PSTE is complex, and an analytical procedure is not yet available to determine the relative concentrations of the mono-, di-, and TG ETO. However, composition was estimated based on fatty acid soap content (level of saponification) and stoichiometry. If we assume the relative reactivities of each glyceride ethoxylate to saponification are equal and that saponification occurs equally and at the same rate with mono-, di-, and TG ETO, then a statistical distribution of molecules can be calculated as a function of the extent of saponification, as shown in Figure 2. Based on the level of saponification as measured by the concentration of fatty acid soap present, compositions for each PSTE can be calculated, as given in Tables 3 and 4. For example, with the Coco 70-1.6 PSTE composition it is estimated to be 16.6% soap, 19.3% ethoxylated glycerol, 21.5% monoglyceride ethoxylate, 26.5% diglyceride ethoxylate, and 16.1% TG ETO.

To confirm the validity of the base assumption that the relative reactivities of each glyceride to saponification are equal, the calculated levels of ethoxylated glycerol were compared to the levels actually measured by liquid chromatography, as given in Table 5. As shown, calculated levels of ethoxylated glycerol are fairly close, but generally higher than measured values. Slightly higher values were expected; however, since the analytical procedure to mea-

TABLE 1
Triglycerides Used in Study

Triglyceride	Source of triglyceride	Molecular weight (by saponification number)	Triglyceride hydrogenated? (yes/no)	Free fatty acid in triglyceride (%)	Iodine value	Refined and bleached (yes/no)
Coconut oil	C+T Quincy (Richmond, VA)	700	Yes	0.05	4	Yes
Tallow	Chemol (Greensboro, NC)	867	No	<1	60–75	Yes
Palm kernel oil	C+T Quincy (Richmond, VA)	727	Yes	0.05	4	Yes

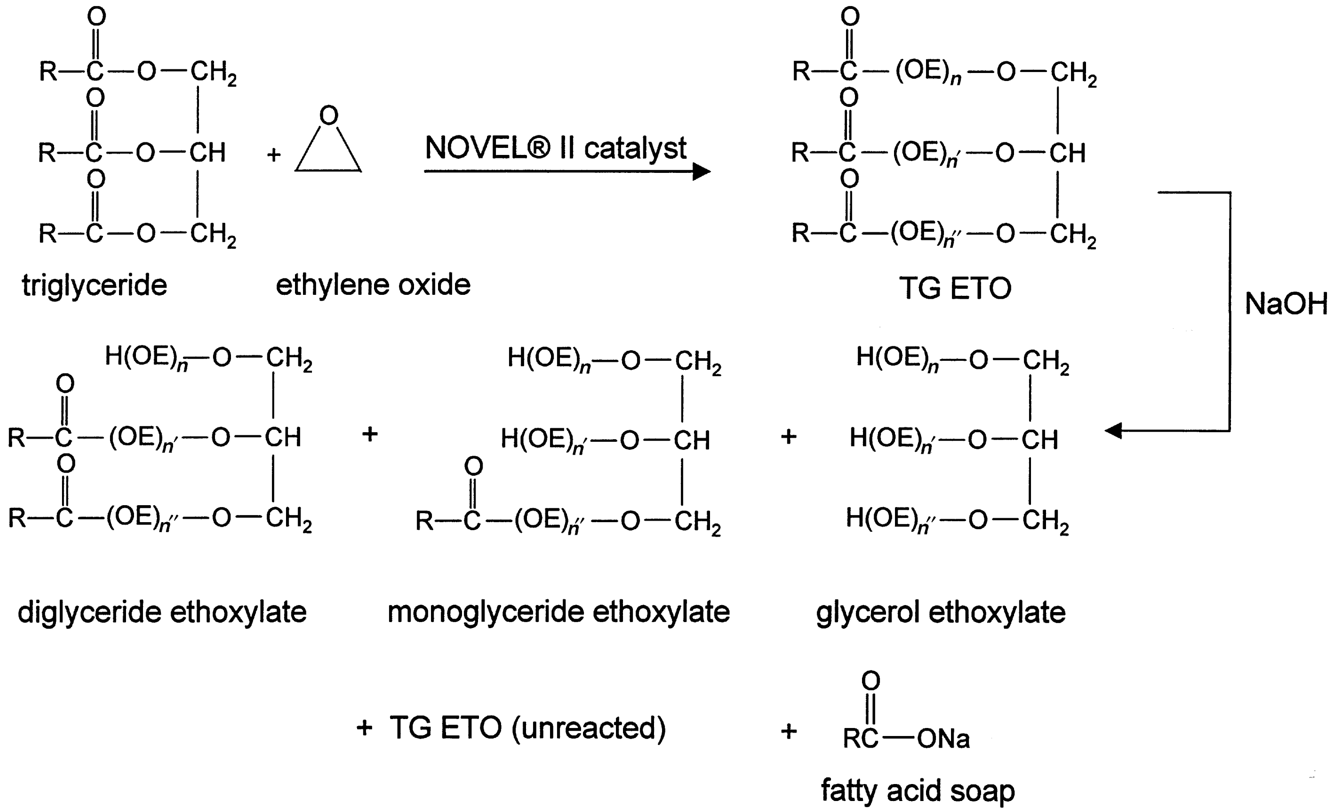

FIG. 1. Preparation of partially saponified triglyceride ethoxylate (TG ETO).

sure ethoxylated glycerol also measures polyethylene glycol content, which is typically in the 1–2% range.

Based on steric factors and the relative capacities of the ethoxylated glycerides to react with sodium hydroxide, one could expect that the triglyceride would be less reactive to base (more difficult to saponify) than diglyceride ethoxylate, and the diglyceride ethoxylate would, in turn, be less reactive to base than the monoglyceride ethoxylate. The analysis given above suggests that this is not true.

Surface activity of PSTE. Gibbs' plots (surface tension vs. log concentration) for the PSTE and reference surfactants are shown in Figures 3 and 4. As shown, all PSTE have similar surface activity. Critical micelle concentrations (CMC) are *ca.* 100 ppm, and surface activity at the CMC is in the 31 to 34 mN/m range. These plots are conventional in shape, showing a distinct CMC.

In contrast, the reference surfactants (Ivory® bar, Dove® bar, and acyl isethionate) yield plots that do not have distinct CMC. In general, it appears the PSTE, as a class, are more efficient as surfactants at lower concentrations, have distinct CMC but are less effective than the reference surfactants in terms of lowering surface tension at relatively high concentrations. It is important to note, however, that a relatively narrow range of PSTE has so far been tested, and it is premature to predict the impact of composition (level of ethoxylation, molecular weight, and unsaturation in the triglyceride, and degree of saponification) on performance.

Physical properties of PSTE. Physical properties for PSTE are given in Table 6. Melting points for PSTE are in the 50–51°C range, which is substantially lower than those of the reference surfactants. In terms of bar hardness, PSTE were found to be softer than acyl isethionate and the acyl isethionate-based bar soap (Dove® bar) but are similar in hardness to the Ivory® soap bar. In terms of foam stability, PSTE produce less foam than acyl isethionate and are con-

TABLE 2
Preparation of Partially Saponified Triglyceride Ethoxylates[a]

Sample description	Degree of ethoxylation (wt.%)	Degree of ethoxylation (mole)	Degree of saponification	Myristic acid added as caustic quench (wt%)
Coco 70-1.6 PSTE	70	23.9	1.6	0.8
Tallow 60-1.6 PSTE	60	29.6	1.6	0.7
Tallow 60-1.9 PSTE	60	29.6	1.9	0.6
PKO 60-1.6 PSTE	60	24.8	1.6	0.7

[a] PKO, palm kernel oil; PSTE, partially saponified triglycerides ethoxylates.

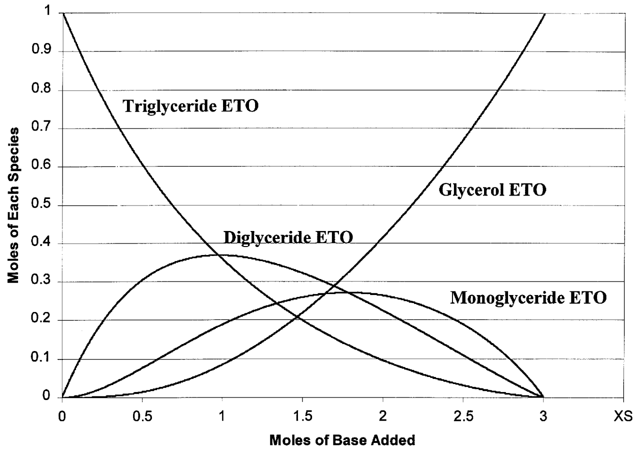

FIG. 2. Theoretical composition of partially saponified triglyceride ethoxylates (PSTE) based on equivalent reactivities of mono-, di-, and triglyceride ethoxylates (ETO) to base.

sidered "low foamers." However, PSTE were observed to "lather" very well, comparable to what is expected from a normal soap bar. PSTE had a light cream color and little odor.

Mildness properties of PSTE. Mildness was examined using two methods. The first method involved measuring the impact of each test material on the health of a luminescent salt water-based bacteria (Microtox^{TM} test).

Microtox^{TM} test results are shown in Table 7. Test results are given as EC_{50} values, which is the concentration at which the surfactant kills 50% of the bacteria (reduces luminescence by 50%). As shown, values obtained with the coconut- and palm kernel oil-based PSTE, and reference surfactants are similar. Values obtained with the tallow PSTE, however, are two orders of magnitude higher, suggesting that they are exceptionally mild and nontoxic.

The mechanism underlying the decrease in toxicity observed for the tallow PSTE is unknown. However, previous studies in our laboratory with the Microtox^{TM} test also showed that larger hydrophobes typically result in decreased toxicity (33).

To confirm mildness, the tallow 60-1.6 PSTE and two reference surfactants were sent for human patch tests. Also tested were the parent TG ETO (before saponification) and blends of both the PSTE and the nonsaponified TG ETO with sodium lauryl sulfate. Results (Table 7) show that the tallow PSTE and the parent ethoxylate are significantly

TABLE 3
Molecular Weights Used in Calculations[a]

Sample description	Molecular weight of triglyceride (by saponification number)	Molecular weight of ethoxylated triglyceride (calculated)	Molecular weight of PSTE (calculated)	Molecular weight of polyethylene glycol (calculated)	Molecular weight of monoglyceride ethoxylate (calculated)	Molecular weight of diglyceride ethoxylate (calculated)	Molecular weight of soap produced during saponification (calculated)
Coco 70-1.6 PSTE	700	2,333	2,399	1,725	1,928	2,131	243
Tallow 60-1.6 PSTE	867	2,168	2,233	1,393	1,651	1,910	298
Tallow 60-1.9 PSTE	867	2,168	2,246	1,393	1,651	1,910	298
PKO 60-1.6 PSTE	727	1,818	1,881	1,183	1,395	1,606	252

[a]See Table 2 for abbreviations.

TABLE 4
Theoretical Composition of PSTE[a]

Sample description	Fatty acid soap content (wt%/measured)	Ethoxylated glycerol (polyethylene glycol) content (wt%/calculated)	Monoglyceride ethoxylate content (wt%/calculated)	Diglyceride ethoxylate content (wt%/calculated)	Triglyceride ethoxylate content (wt%/calculated)
Coco 70-1.6 PSTE	16.6	19.3	21.5	26.5	16.1
Tallow 60-1.6 PSTE	21.7	16.1	19.7	25.9	16.7
Tallow 60-1.9 PSTE	25.7	23.9	19.7	20.4	10.4
PKO 60-1.6 PSTE	21.0	15.3	19.6	26.5	17.6

[a]Assuming equal reactivities of mono-, di-, and triglyceride ethoxylate to saponification; using molecular weights given in Table 3. See Table 2 for abbreviations.

TABLE 5
Comparison of Theoretical vs. Measured Ethoxylate and Glycerol Content[a]

Sample description	Ethoxylated glycerol (polyethylene glycol) content (wt%/from Table 4)	Ethoxylated glycerol (polyethylene glycol) content (wt%/measured)
Coco 70-1.6 PSTE	19.3	14.6
Tallow 60-1.6 PSTE	16.1	18.1
Tallow 60-1.9 PSTE	23.9	22.9
PKO 60-1.6 PSTE	15.3	13.5

[a]See Table 2 for abbreviations.

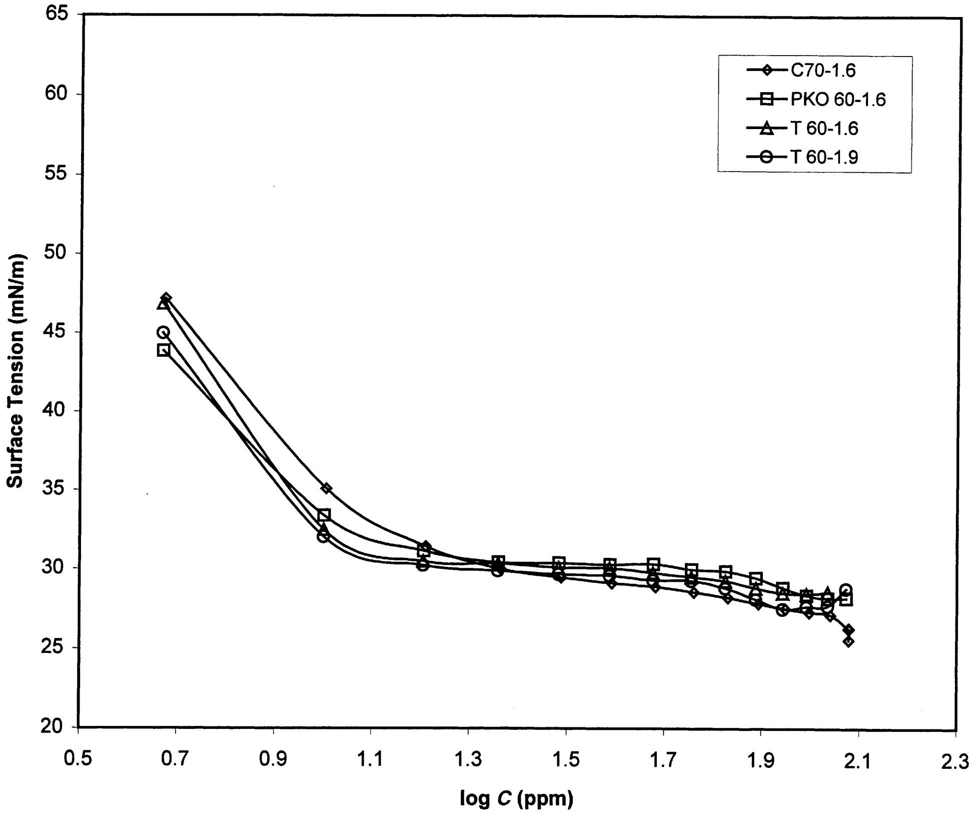

FIG. 3. Gibbs' plots of PSTE. For sample descriptions see Table 3. See Figure 2 for abbreviation.

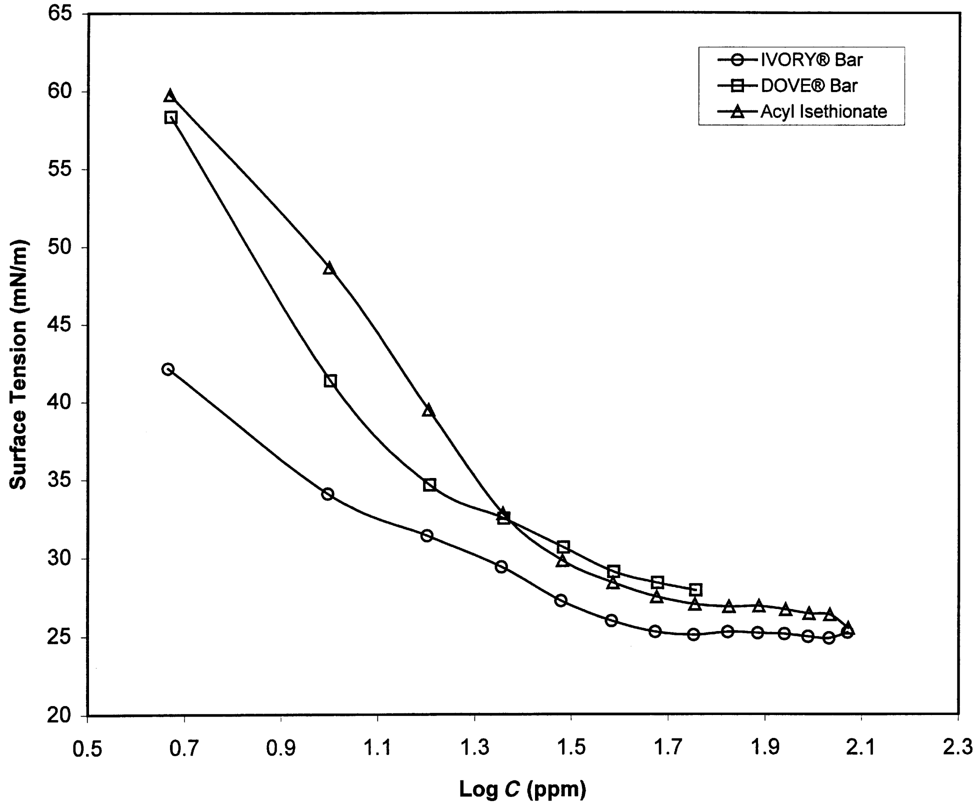

FIG. 4. Gibbs' plots of reference surfactants.

TABLE 6
Physical Properties of Partially Saponified Triglyceride Ethoxylates and Reference Surfactants

		Shore hardness		Foam height (mL)	
	Melting point (°C)	Instantaneous (avg. 5 values)	15-s delay (avg. 5 values)	Without soil (avg. 4 values)	With soil[a] (avg. 4 values)
Sample description					
Coco 70-1.6 PSTE	51	7	4	125	110
Tallow 60-1.6 PSTE	51	2	2	110	110
Tallow 60-1.9 PSTE	51	1	0	120	110
PKO 60-1.6 PSTE	50	0	0	133	113
Reference surfactants					
Acyl isethionate	~235	83	83	270	193
Conventional synthetic bar soap (Dove®)	~135	59	42	150	120
Conventional Bar Soap Ivory®)	~265	6	6	110	110

[a] 15% Crisco Shortening, 15% olive oil, 15% instant mashed potato flakes, 30% milk, 25% water. See Table 2 for abbreviations. Dove, Lever Brothers Co. (New York, NY); Ivory, Procter & Gamble (Cincinnati, OH).

TABLE 7
Mildness Properties of Partially-Saponified Triglyceride Ethoxylates and Reference Surfactants

	Microtox test results	Human patch test results	
Sample Description	(EC_{50} in mg/L)	Numerical score[a]	Classification
Coco 70-1.6 PSTE	14.1, 8.0	Not tested	—
Tallow 60-1.6 PSTE	1622.0, 1101.0	55	"Probably mild"
Tallow 60-1.9 PSTE	1034.0, 1237.0	Not tested	—
PKO 60-1.6 PSTE	15.3	Not tested	—
Tallow 60 triglyceride ethoxylate (parent of Tallow 60-1.6 PSTE)		113	"Probably mild"
Reference surfactants			
Acyl isethionate	31.9, 15.7	302	"Experimental cumulative irritant"
Conventional symthetic bar soap (DOVE)	21.4, 24.4	Not tested	—
Conventional bar soap (IVORY)	10.8, 6.3	Not tested	—
Sodium Lauryl Sulfate	0.3	405	"Experimental primary irritant"
1:1 Blend (by wt.) of Tallow 60 triglyceride ethoxylate + sodium lauryl sulfate	Not tested	328	"Experimental cumulative irritant"
1:1 Blend (by wt.) of Tallow 60-1.6 PSTE + Sodium Lauryl Sulfate	Not tested	302	"Experimental cumulative irritant"

[a] Higher volume = higher irritation. See Table 1 for abbreviations and Table 6 for company addresses.

milder than the reference acyl isethionate. Furthermore, both the PSTE and its parent ethoxylate improved the mildness properties of alcohol sulfate, which suggests that both materials may have potential as mildness improvement agents.

Mildness properties of PSTE suggest their application in personal-wash products, perhaps as a less costly alternative to acyl isethionate. Since they also contain large alkyl groups, they could also find application as emulsifiers in personal-care and cosmetic products. In addition, the potential for PSTE to amend the mildness properties of other surfactants suggests their use as a co-surfactant in products requiring mildness, such as dishwashing liquids.

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