Methyl Ester Ethoxylates[1]

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ABSTRACT: Conventional ethoxylation of fatty methyl esters, or other fatty-fatty esters or diesters, produces poor yields of the desired ethoxylated ester. A proprietary ethoxylation catalyst, currently in use to produce "peaked" or "narrow-range" alcohol ethoxylates, has been found to successfully insert ethylene oxide into the ester linkage of fatty esters. The mechanism for this insertion likely involves an ethoxylation–transesterification step in the ethoxylation process. Physical, performance, and environmental/human safety properties were evaluated. Results, in general, show that methyl ester ethoxylates behave similarly to alcohol ethoxylates with the exception of having a lower foam profile and being less irritating.
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KEY WORDS: Detergency, ethoxylated methyl esters, fatty methyl ester ethoxylate, foaming, hard-surface cleaning, methyl ester ethoxylates, performance, physical properties.

Over three million metric tons of ethylene oxide (EO)-derived surfactants are consumed annually in the world today (1). As shown in Table 1, more than half of this volume involves the ethoxylation of linear alcohols (mostly based on petrochemical feedstocks), while the remainder consists of ethoxylated phenols, alkoxides, and various amines. Structurally, conventional ethoxylation feedstocks carry an "active" hydrogen connected to a hetero-atom, such as oxygen and nitrogen. This hydrogen atom can easily be removed to form a reactive anion, which is essential for conventional ethoxylation to take place.

During the past decade or so, the most significant development in the EO-derived surfactant arena has been the development of novel ethoxylation catalysts that provide a more "peaked" or "narrow-range" distribution of ethoxymers (Fig. 1). These catalysts bring about "peaking" by altering the relative reactivity of the unethoxylated feedstock vs. the ethoxymers (2). Development of these new catalysts has expanded the range of EO-derived surfactants as a consequence of their ability to ethoxylate feedstock molecules that do not carry an active hydrogen, such as methyl esters, fatty-fatty diesters, and triglycerides.

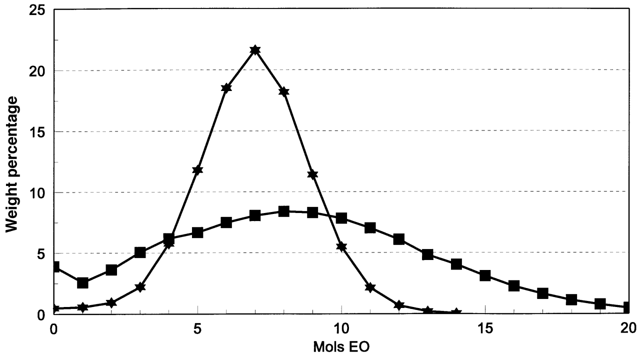

FIG. 1. Ethoxylation of dodecanol: ■, conventional catalyst; ✶, proprietary catalyst.

Methyl ester ethoxylates are receiving significant attention, as demonstrated by recent patents and publications (3–9). The driving force for this attention is twofold: methyl esters are major items of commerce available from triglyceride oils and from the esterification of fatty acids. The addition of methyl ester ethoxylates also gives detergent manufacturers another choice from the ethoxylate menu.

This study discusses the ethoxylation chemistry, and the physical, performance, and environmental/human safety properties of methyl ester ethoxylates. Because methyl ester ethoxylates are similar in composition to alcohol ethoxylates (Fig. 2), the performance of "peaked" alcohol ethoxylates is also included for reference purposes.

EXPERIMENTAL PROCEDURES

Ethoxylation of methyl esters. Ethoxylation of methyl esters with conventional hydroxide catalysts (NaOH, KOH,

TABLE 1
Estimates of Current Worldwide Production of Ethoxylates[a]

Current ethoxylate production	Metric tons (thousands)
Alcohol ethoxylates	~750
Alcohol ether sulfates	~750
Alkylphenol ethoxylates	~600
Ethoxylated nitrogen compounds[b]	~50
EO/propylene oxide block copolymers	~50

[a]Reference 1; EO, ethylene oxide.
[b]Not including alkanolamides.

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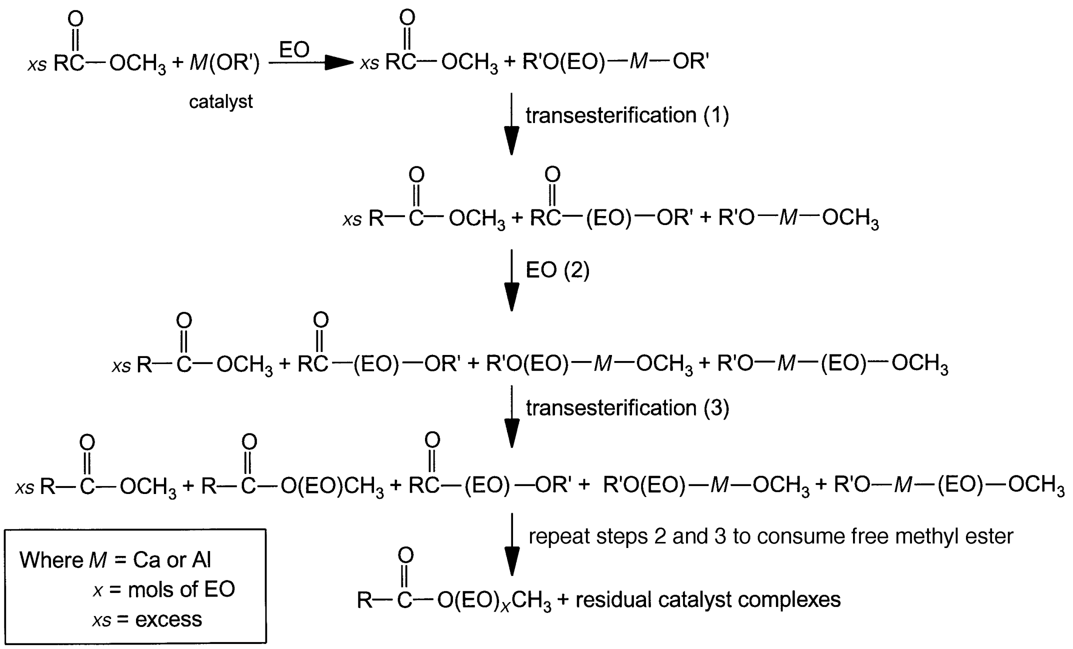

SCHEME 1

TABLE 2
Carbon Chain Distributions of Methyl Esters and Alcohols Used in Study

	Weight percentage						
Carbon chainlength	Lauryl-range[a] methyl ester	Tallow-range methyl ester	C_8 methyl ester	C_{14} methyl ester	Lauryl-range alcohol	Tallow-range alcohol	C_{610} alcohol
C_6	—	—	—	—	—	—	18
C_8	—	—	>99	—	—	—	38
C_{10}	—	—	—	—	—	—	44
C_{12}	54	<1	—	—	67	—	
C_{14}	22	<1	—	>99	25	<1	
C_{16}	11	32	—	—	7	32	
C_{18}	13	66	—	—	<1	66	
Molecular weight	~223	~274	~144	~228	~197	~260	~137

[a] "Stripped" version was used ("unstripped" version contains C_8 and C_{10} methyl esters).

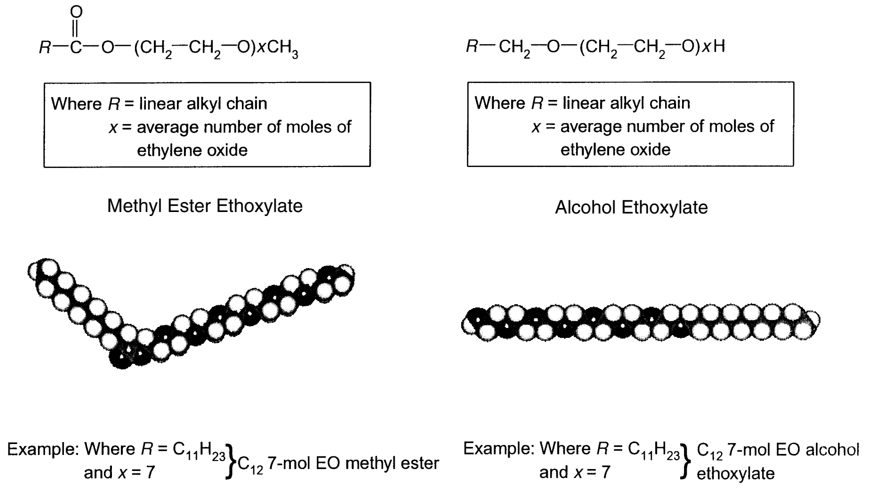

FIG. 2. Visual comparison of C_{12} 7-mol methyl ester and alcohol ethoxylate. See Figure 1 for abbreviation.

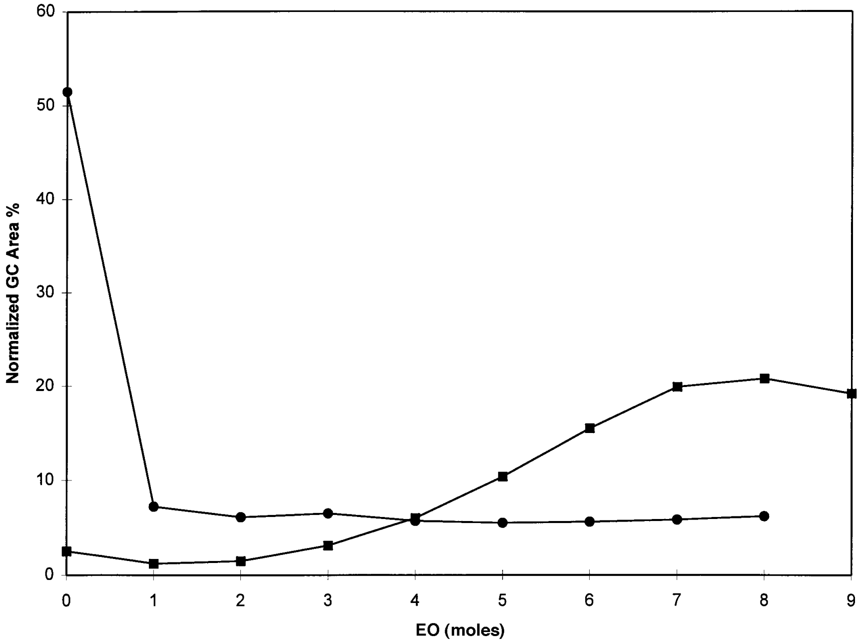

FIG. 3. Ethoxymer distributions for tetradecyl-60% methyl ester ethoxylate prepared with NaOH (conventional catalyst) and proprietary catalyst [by gas chromatography (GC)]: ●, conventional catalyst; ■, proprietary catalyst. See Figure 1 for other abbreviation.

etc.) does not proceed well because of the absence of an active hydrogen (Fig. 3). Conversion is relatively poor, with a significant residue of unethoxylated methyl ester and a broad distribution of ethoxymers.

Ethoxylation of methyl esters with a more active proprietary catalyst was significantly more successful in reducing the level of unethoxylated methyl ester and in obtaining a more "peaked" distribution of ethoxymers (Fig. 3). The

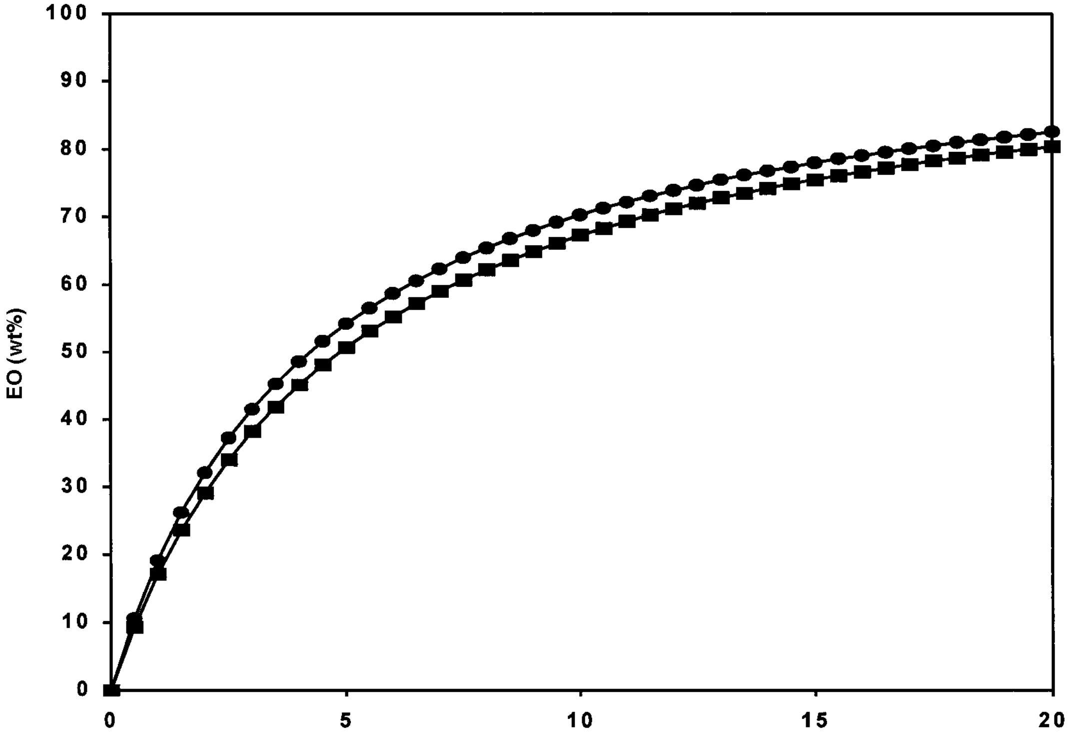

FIG. 4. Relationship between moles EO and EO (wt%) for methyl ester ethoxylate and alcohol ethoxylate: ●, C_{12} alcohol ethoxylate; ■, C_{12} methyl ester ethoxylate. See Figure 1 for abbreviation.

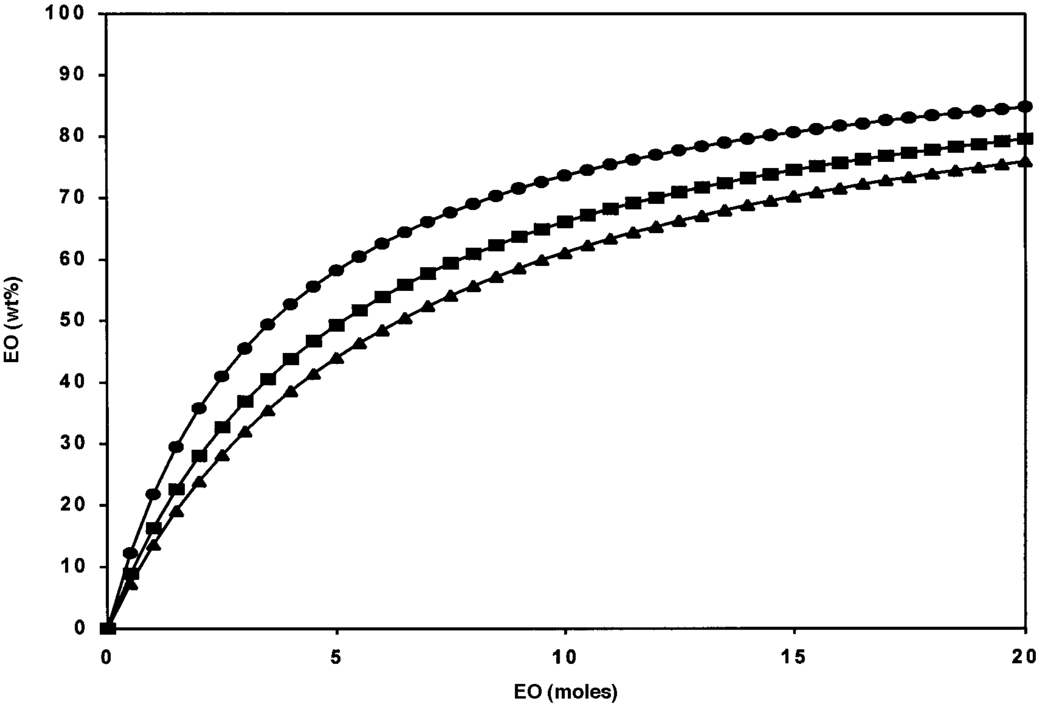

FIG. 5. Relationship between moles EO and EO (wt%) for methyl ester ethoxylate: ●, octyl methyl ester ethoxylate; ■, lauryl-range methyl ester ethoxylate; ▲, tallow-range methyl ester ethoxylate. See Figure 1 for abbreviation.

ethoxylation catalyst used consists of a calcium and aluminum complex that is partially neutralized in an alcohol ethoxylate base (10). The catalyst itself is approximately five times more active than conventional hydroxide catalysts. Ethoxylation of methyl esters with this catalyst, however, is still a straightforward single-batch process, which utilizes conventional ethoxylation equipment. Ethoxylations were performed with 1% catalyst (based on the final weight of the catalyst).

The mechanism for ethoxylation is unknown but thought to consist of the process illustrated in Scheme 1. The active

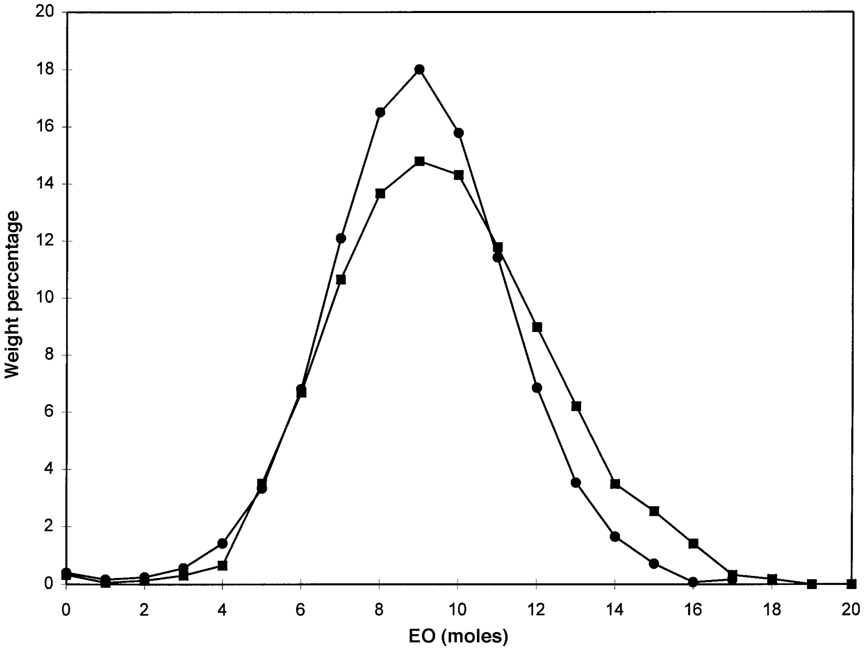

FIG. 6. Ethoxymer distributions for tallow-60% methyl ester ethoxylate and alcohol ethoxylates (by high-pressure liquid chromatography): ■, methyl ester ethoxylate; ●, alcohol ethoxylate. See Figure 1 for abbreviation.

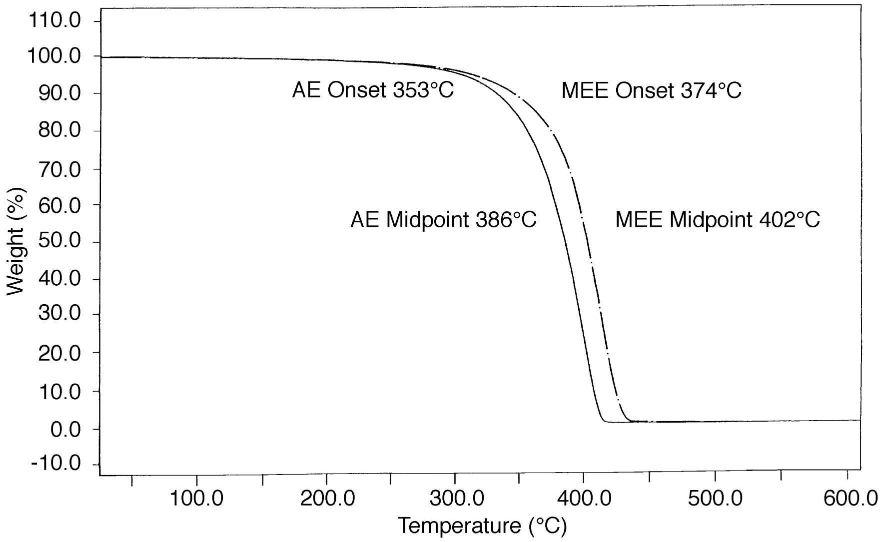

FIG. 7. Thermal analysis profiles for lauryl-65% methyl ester (MEE) and alcohol ethoxylates (AE).

catalyst (calcium and aluminum alkoxyethoxylate) first reacts with EO to form the ethoxylated version of the metal alkoxyethoxylate, which can then transesterify with methyl ester to form the alkyl ester ethoxylate and a metal-coordinated methoxide ion. The addition of more EO (step 2) produces ethoxylated versions of the metal-coordinated methoxide ions, which can then transesterify the ester (step 3) to form methyl ester ethoxylate, alkyl ester ethoxylate, and metal-coordinated methoxides. Steps 2 and 3 occur continuously with the addition of more EO until the excess methyl ester is consumed to produce a distribution of methyl ester ethoxylates that contain a small concentration of residual catalyst complexes.

Compositional variables, such as unsaturation and carbon chainlength distribution, do not appear to influence the ethoxylation reaction or overall ethoxylate quality. The purity of the methyl ester, however, does appear to impact color, as described later in this paper.

Samples. Methyl ester ethoxylate samples used in this study were made from lauryl-range, tallow-range, or single homolog methyl esters (C_8 and C_{14} methyl esters). Carbon chainlength distributions for these methyl esters, as well as for the alcohols used to prepare reference alcohol ethoxylates, are shown in Table 2. Please note that, with the exception of the tallow-range materials, methyl ester–alcohol ethoxylate pairs do not match exactly in terms of carbon chain distribu-

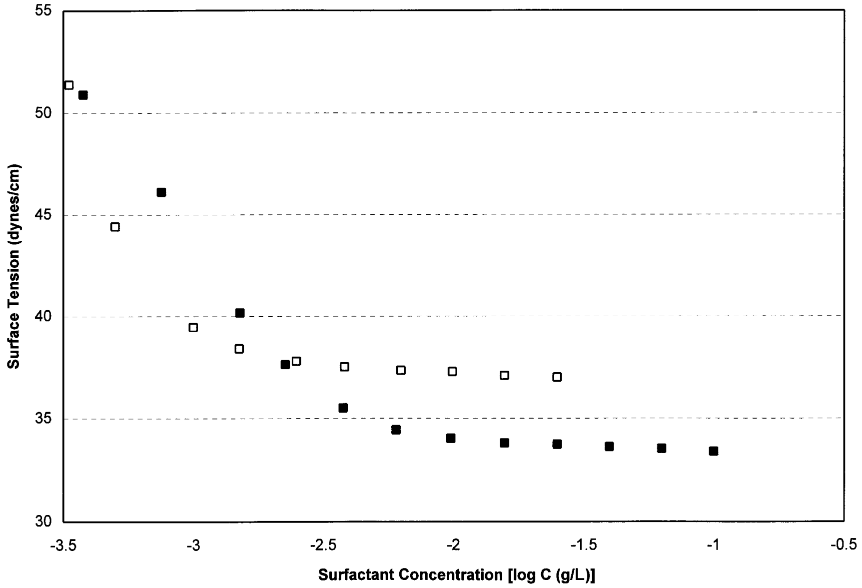

FIG. 8. Gibbs' plots (surface tension vs. surfactant concentration) of lauryl methyl ester ethoxylate (MEE) vs. alcohol ethoxylate (AE): ■, lauryl-65% MEE; □, lauryl-65% AE.

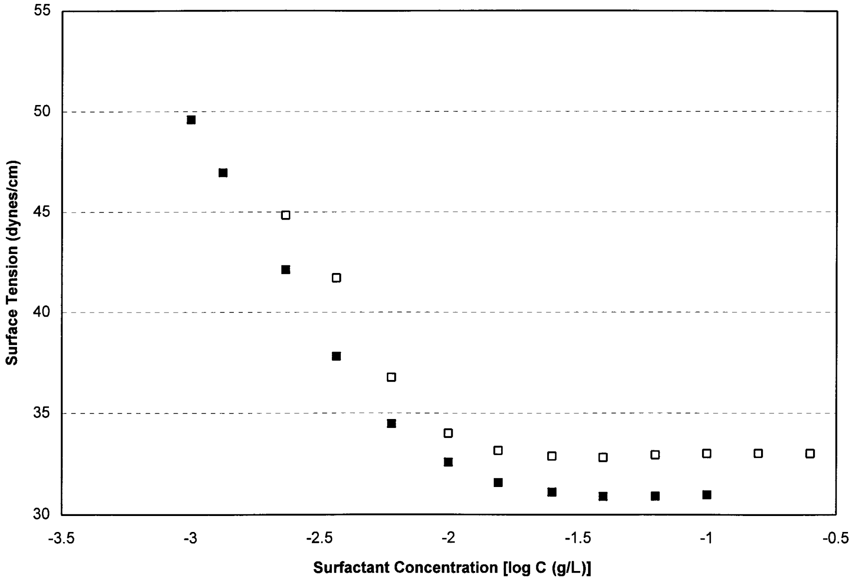

FIG. 9. Gibbs' plots (surface tension vs. surfactant concentration) of tallow methyl ester ethoxylate (MEE) vs. alcohol ethoxylate (AE): ■, tallow-65% MEE; □, tallow-65% AE.

tion but were considered acceptable for the objectives of this study.

The relationship between EO content and water solubility is well understood for alcohol ethoxylates. When expressed in terms of average weight percentage (the amount of EO added to make the alcohol ethoxylate on an average weight percentage basis), an ethoxylate is generally water-soluble if EO content is above 50%, and oil-soluble if it is below 50% (50% ethoxylates are considered borderline water-soluble).

With methyl ester ethoxylates, however, the level of EO necessary to reach the boundary between water insolubility and water solubility is likely higher due to the terminal methyl group. Replacing the terminal hydroxyl group with a methyl group adds hydrophobicity to the EO chain, which would reduce water solubility. Consequently, only methyl ester ethoxylates that contain an average of 55% or greater EO content were examined in this study.

TABLE 3
Ethylene Oxide Content of Samples Used in Study

Sample description	Average weight percentage EO[a]	Average moles EO
Tetradecyl-60% methyl ester ethoxylate	60	7.8
Lauryl-55% methyl ester ethoxylate	55	6.2
Lauryl-60% methyl ester ethoxylate	60	7.6
Lauryl-65% methyl ester ethoxylate	65	9.4
Lauryl-70% methyl ester ethoxylate	70	11.8
Tallow-65% methyl ester ethoxylate	65	11.5
Lauryl-65% alcohol ethoxylate	65	8.3
Tallow-65% alcohol ethoxylate	65	11
Std. 9-mol nonylphenol ethoxylate	~65	9–10
Std. C_{6-10}-50% alcohol ethoxylate	50	3.1

[a] Within ± 1% as measured by nuclear magnetic resonance spectroscopy. See Table 1 for abbreviation.

As with all ethoxylates, the relationship between moles of EO and weight percentage EO is nonlinear for methyl ester ethoxylates. This relationship is also slightly different than for the corresponding alcohol ethoxylate because of the difference in molecular weight between the feedstocks (Fig. 4). The relationship between moles of EO and weight percentage EO for octyl, lauryl-range, and tallow-range methyl ester ethoxylates is shown for reference in Figure 5.

Another variable to consider when comparing methyl ester ethoxylates to alcohol ethoxylates is the ethoxymer distribution. As shown in Figure 6, alcohol ethoxylates are slightly more peaked than their methyl ester counterparts, even though the methyl ester–alcohol pairs were prepared with the same catalyst.

Another difference between methyl ester ethoxylates and alcohol ethoxylates pertains to unsaturation. Methyl esters, particularly tallow-range, have a significant degree of unsaturation (generally greater than 50%). Alcohols, in general, are fully saturated.

With regard to samples used in this study, average EO content is expressed as weight percentage. Although moles are commonly used to express average EO content, weight percentage EO is a better indication of the hydrophilic nature of the sample and is independent of carbon chainlength. EO contents, expressed in both moles and weight percentage EO, are listed in Table 3.

Chemical stability. Chemical stability was examined at 40°C by monitoring (*via* ^{13}C nuclear magnetic resonance spectroscopy) the stability of buffered 10% solutions of tetradecyl—60% methyl ester ethoxylate at pH 7 and 9.

Thermal stability. Thermal stability was examined by thermogravimetric analysis (Perkin Elmer TGA-7; Norwalk, CT).

Melting point. Melting points were measured in an incubator equipped with a temperature controller and an outer glass door.

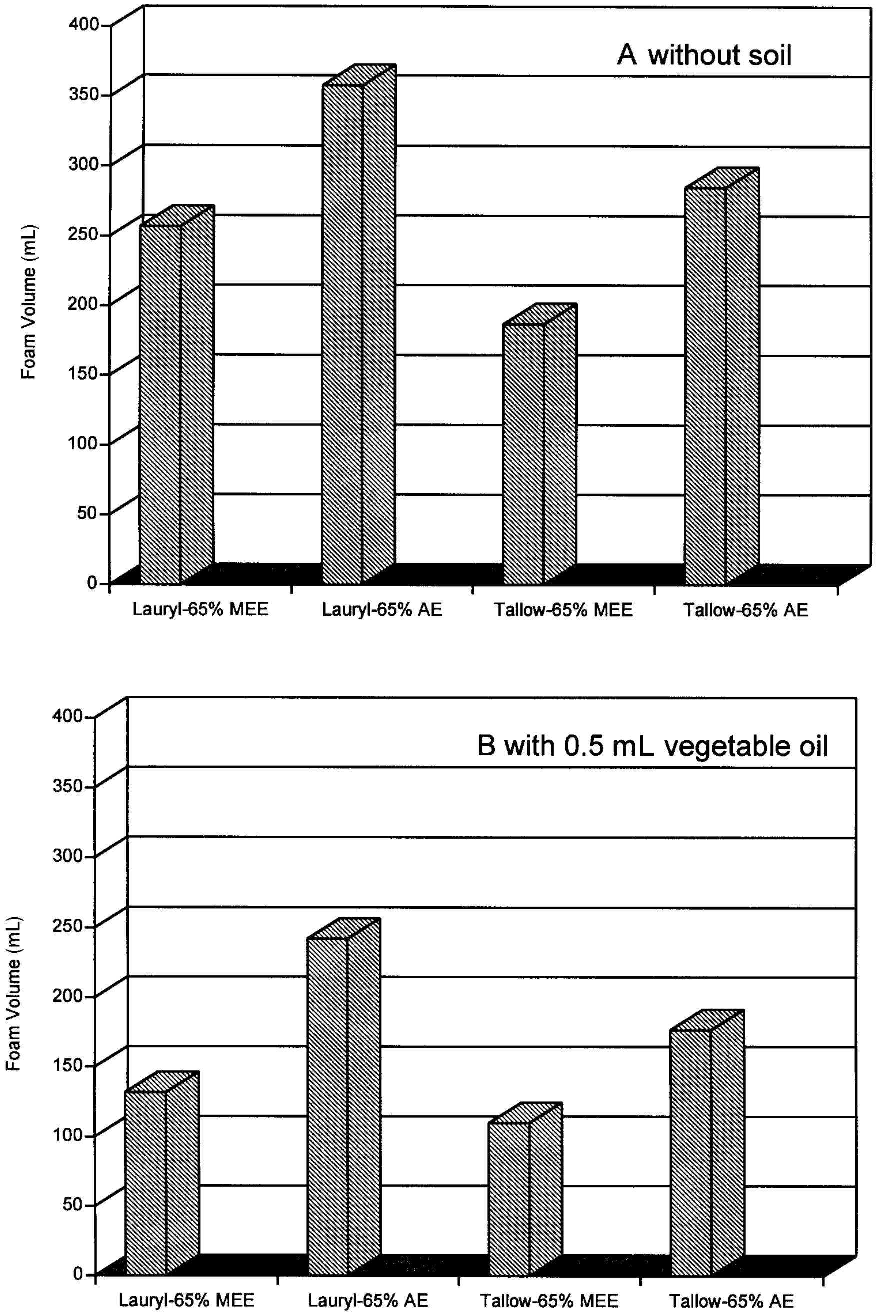

FIG. 10. Flash foam measurements for methyl ester ethoxylate (MEE) and alcohol ethoxylate (AE). For method description, see Reference 10.

Viscosity. Viscosity was examined with a digital viscometer (Brookfield DV-II, model RVTDVCP II, Stoughton, MA).

Water solubility. Water solubility was examined by measuring the inverse cloud point by heating 1% aqueous solutions of the ethoxylate and determining the temperature at which the solution clouds (the "cloud point").

Gibb's plots. Gibb's plots were obtained with a Lauda Automated Tensiometer (model TEIC, distributed by Brinkmann, Westbury, NY).

Foam. Foam was measured with a Schlag foam generation apparatus (manufactured in-house; see Ref. 11).

Detergency performance. Detergency performance was measured by using the protocol, test conditions, and formulation described in Table 4.

Hard-surface cleaning performance. Hard-surface cleaning performance was tested with a Gartner straight-line washability and abrasion machine. It was modified to improve reproducibility and permit simultaneous testing of three different cleaning solutions. Equipment and protocol are described elsewhere (12).

Biodegradability. Biodegradability was examined by means of the "semi-continuous activated sludge" (SCAS) biodegradation test (15).

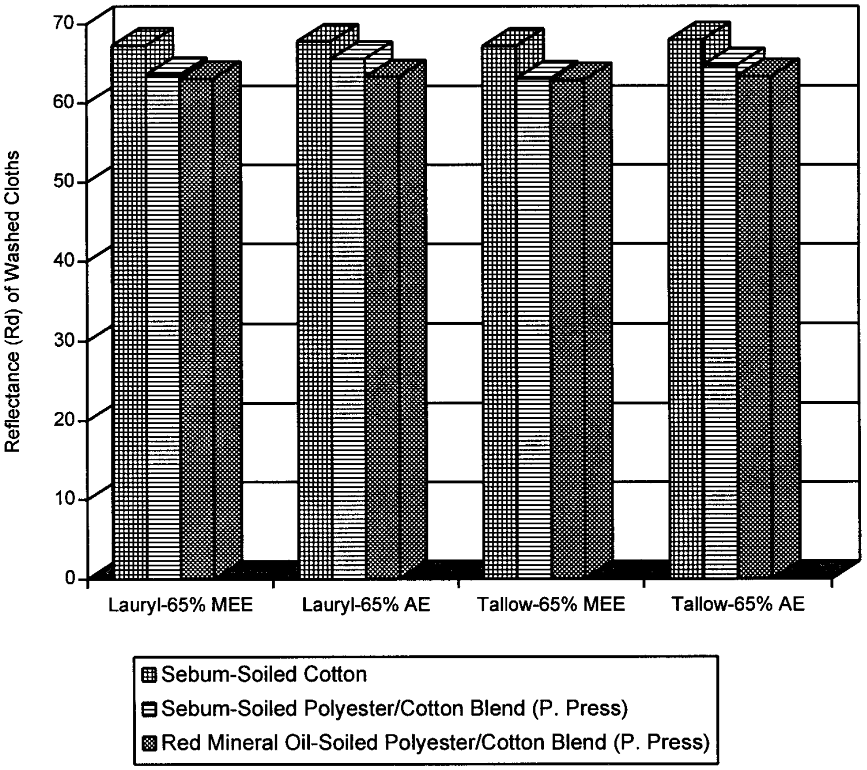

FIG. 11. Detergency performance of lauryl and tallow methyl ester ethoxylate (MEE) and alcohol ethoxylate (AE). See Table 4 for test conditions, protocol, and formulations.

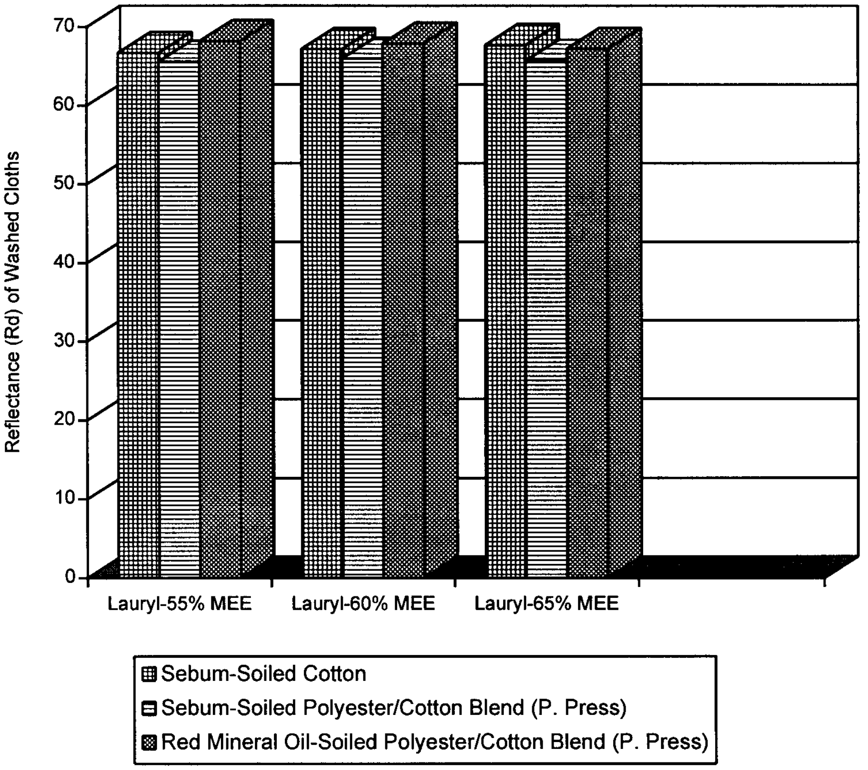

FIG. 12. Detergency performance of lauryl methyl ester ethoxylate (MEE) as function of moles ethoxylate. See Table 4 for test conditions, protocol, and formulations.

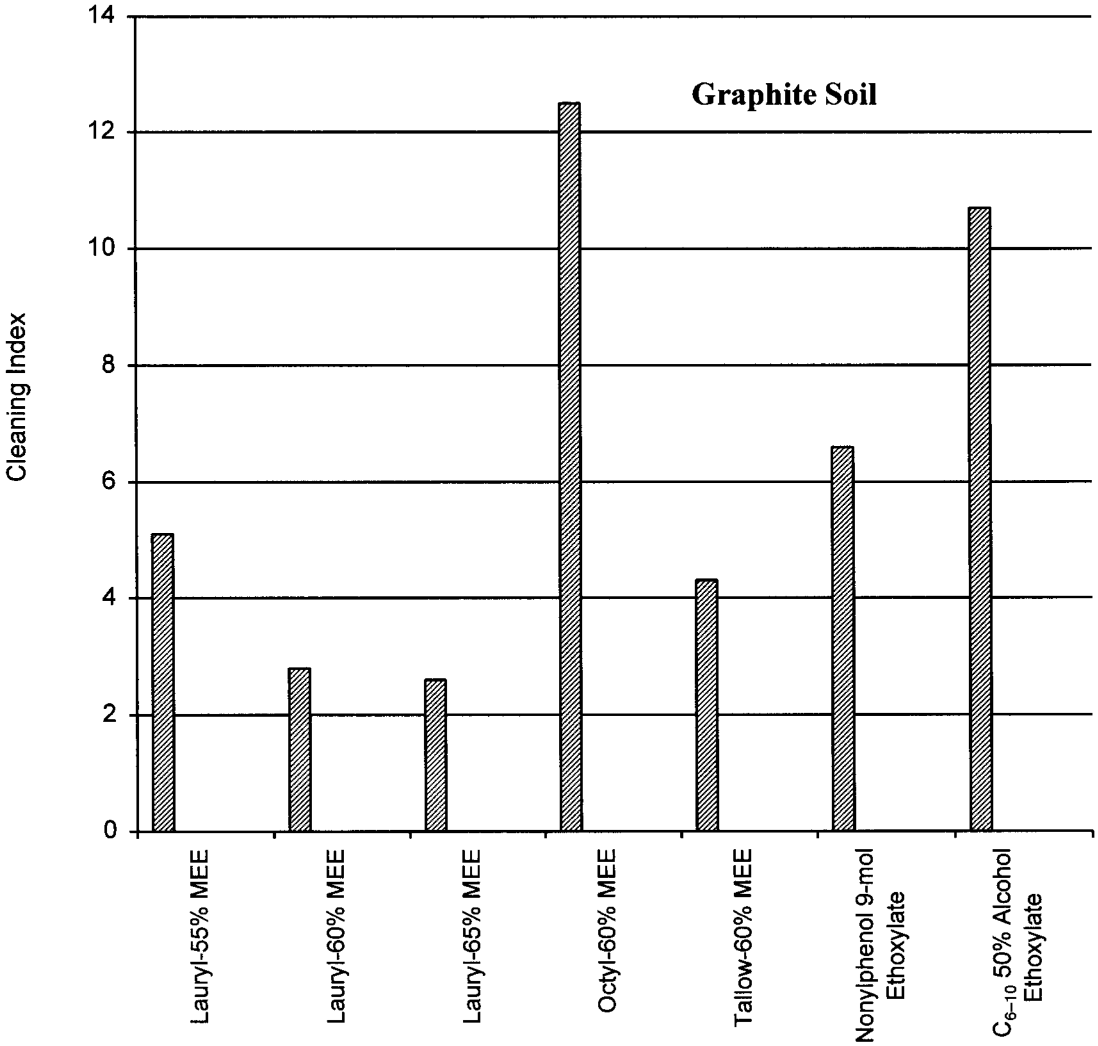

FIG. 13. Hard-surface cleaning performance of methyl ester ethoxylates (MEE). Cleaning index = [(reflectance of cleaned substrate) – (reflectance of soiled substrate)]/number of test strokes.

RESULTS AND DISCUSSION

Chemical stability. The presence of an ester linkage makes methyl ester ethoxylates susceptible to alkaline hydrolysis, unlike their alcohol ethoxylate counterparts. This was examined by monitoring the stability at 40°C of buffered 10% solutions of tetradecyl-60% methyl ester ethoxylate at pH 7 and 9. Results (Table 5) show that, after more than 11 wk at 40°C, 4% decomposition occurred at pH 7 and 13.5% decomposition occurred at pH 9. These results suggest that products containing methyl ester ethoxylates should be formulated at a pH of 9 or below. For most applications, this should not be a problem. The potential for hydrolysis occurring when methyl ester ethoxylates are placed in powder formulations with alkaline ingredients, however, will logically need to be investigated.

The thermal stability of methyl ester ethoxylates vs. alcohol ethoxylates was examined by thermogravimetric analysis. As shown in Figure 7, methyl ester ethoxylate, like alcohol ethoxylate, is thermally stable up to its boiling point range. Compared to their alcohol ethoxylate counterparts, methyl ester ethoxylates appear to have higher boiling points.

Melting point. Melting points for lauryl-range and tallow-range methyl ester ethoxylates and their alcohol ethoxylate counterparts are shown in Table 6. Although there is little difference between the lauryl-range ethoxylates, the tallow methyl ester ethoxylate has a lower melting point than that of the tallow alcohol ethoxylate. Two factors may be involved. First, tallow methyl esters have a higher degree of unsaturation in comparison to lauryl methyl esters, and unsaturation usually lowers melting point. Replacement of the terminal hydroxyl group with a methyl group may also diminish the impact of EO chainlength on the melting point of longer-chain ethoxylates. Regardless, a lower melting point could be of some advantage for tallow-range methyl ester ethoxylates with respect to their storage and handling.

Viscosity. Viscosity was examined for neat ethoxylates as well as for 15 and 30% solutions (see Table 7). As expected, viscosities of the lauryl-range methyl ester and alcohol ethoxylates were low at all concentrations. The tallow-range ethoxy-

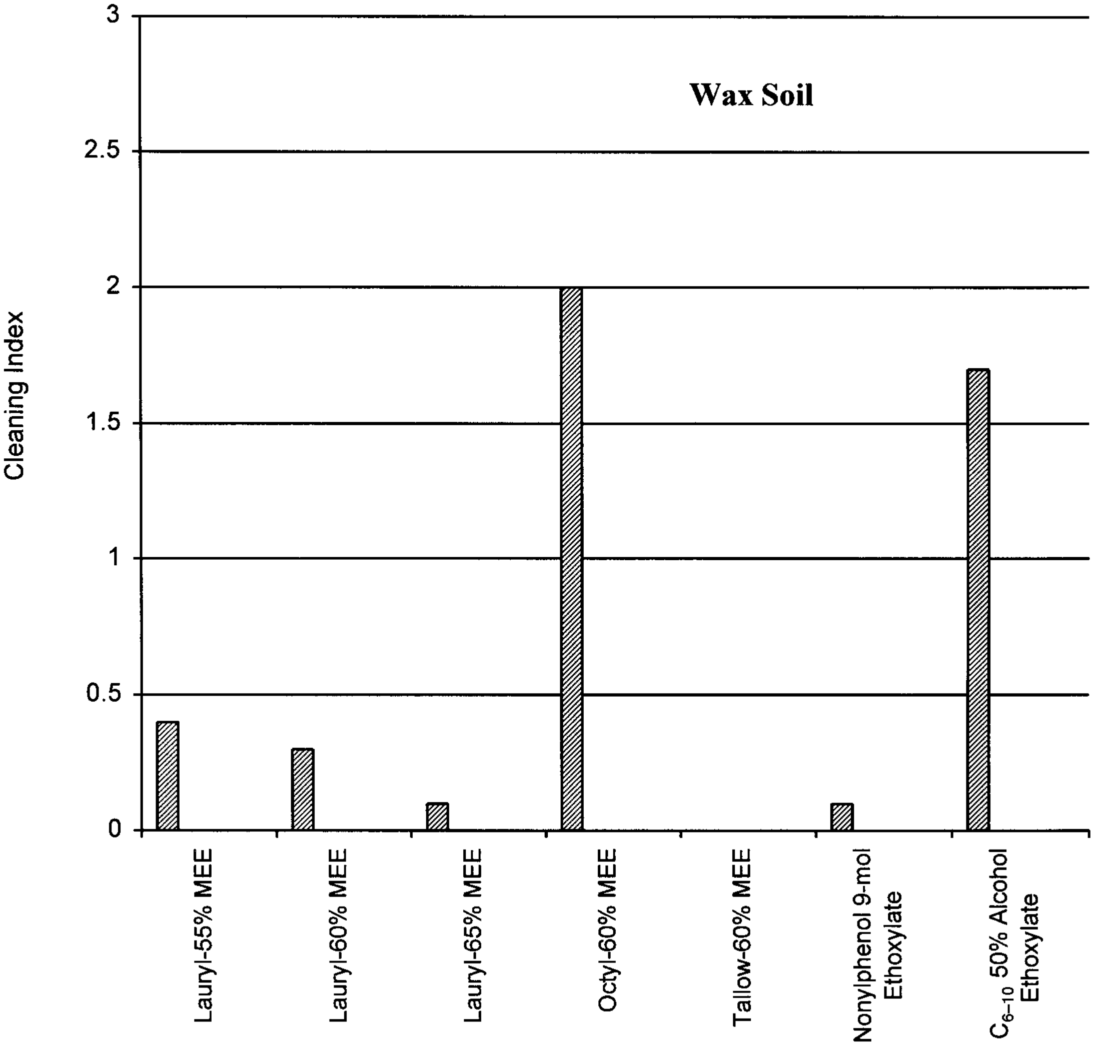

FIG. 14. Hard-surface cleaning performance of methyl ester ethoxylates (MEE). For definition of cleaning index, see Figure 13.

lates, however, did clearly show different viscosity behavior, indicating corresponding differences in phase behavior. Again, differences are likely related to differences in unsaturation and molecular structure. Whether or not these differences translate to an advantage or disadvantage is beyond the scope of this paper and will be examined in detail in a future study.

Water solubility. The solubility of methyl ester ethoxylates, like that of alcohol ethoxylates, is determined by measuring the inverse cloud point. Inverse cloud point is measured by heating a 1% aqueous solution of the ethoxylate, and determining the temperature at which the solution clouds (the "cloud point"). Water solubility of ethoxylates is directly related to the interaction of the EO chain with water molecules. As temperature is increased, hydration of the EO chain decreases. Eventually, the extent of dehydration becomes sufficient for the surfactant to become insoluble, as measured by the appearance of a cloudy solution. A higher inverse cloud point indicates greater water solubility.

Solubility measurements of methyl ester ethoxylates, and their alcohol ethoxylate counterparts, are shown in Table 8. As shown, cloud point measurements for methyl ester ethoxylates are approximately 15–20°C lower than their corresponding alcohol ethoxylate equivalents. Although results also show that methyl ester ethoxylate solubility is easily amended by altering EO content, it does not appear that the addition of more EO completely compensates for the difference in solubility between methyl ester ethoxylate and alcohol ethoxylate. This suggests that the solubility vs. inverse cloud point relationship for methyl ester ethoxylates is different than for alcohol ethoxylates. However, the ease in preparing solutions for testing further suggests that methyl ester ethoxylates and alcohol ethoxylates, in general, have similar solubility vs. EO content characteristics. These relationships will be examined in more depth in future studies.

Surface properties. Gibbs' plots (equilibrium surface tension vs. log of the surfactant concentration) for lauryl-range and tallow-range 65% methyl ester ethoxylates and alcohol ethoxylates are shown in Figures 8 and 9. At equal weight percentage EO, methyl ester ethoxylates have a substantially

TABLE 4
Detergency Test Materials and Procedures

Testing apparatus	Terg-O-Tometer	
Wash cycle	10 min	
Rinse cycle	5 min	
Wash temperature	100°F (37.8°C)	
Water hardness	100 ppm (as $CaCO_3$; 2:1 Ca/Mg)	
Alkalinity	25 ppm NaOH	
Surfactant concentration	150 ppm	
Soil/substrates	Sebum/cotton and Sebum/permanent press—manufactured in-house with synthetic sebum[a]; Cotton (Test Fabrics S/419); Permanent press (Test Fabrics S/7406-65% Dacron/35% cotton with permanent press finish) Mineral oil/permanent press—manufactured in-house by using mineral oil with oil-soluble red dye to aid with detection; Permanent press (Test Fabrics S/7406)	
Number soiled cloths	Three 4.5″ × 3.25″ swatches of sebum/cotton and sebum/permanent press cloths washed together with three clean cotton cloths added for ballast; three 4.5″ × 3.25″ swatches of mineral oil/permanent press cloths washed with six clean cotton cloths added for ballast; three 4″ × 3″ swatches of clay/permanent press cloth washed with six clean cloths added for ballast	
Reflectance measuring device	Hunter D25A (Reston, VA) Colorimeter	
Synthetic sebum component	Source	wt%
Palmitic acid	Kodak (Rochester, NY)	10.0
Stearic acid	Kodak (Rochester, NY)	5.0
Coconut oil	Sargent-Welch (Skokie, IL)	15.0
Paraffin wax	Generic	10.0
Spermaceti wax	Sargent-Welch (Skokie, IL)	15.0
Olive oil	Generic	20.0
Squalene	Kodak (Rochester, NY)	5.0
Cholesterol	Kodak (Rochester, NY)	5.0
Oleic acid	Kodak (Rochester, NY)	10.0
Linoleic acid	Kodak (Rochester, NY)	5.0

[a] Soil recipe consists of 67.6% synthetic sebum (below), 16.2% particulate dust, 10.8% triethanol amine, and 5.4% oleic acid, based on recipe given by Spangler, W.G., H.D. Cross, and B.R. Schaafsma, *J. Am. Oil Chem. Soc. 42*:723 (1965).

higher critical micelle concentration (CMC), but a lower surface tension at or beyond the CMC.

Differences in surface properties between methyl ester ethoxylates and alcohol ethoxylates are logically related to structure. The increase in CMC is likely due to the presence of the ester carbonyl moiety, which adds rigidity and steric bulk to the methyl ester ethoxylate molecule. An increase in rigidity and bulk would likely reduce the tendency to micellize, leading to a higher CMC.

The lower surface tension of methyl ester ethoxylates at or beyond the CMC is similarly related to structure, but with respect to the terminal methyl group on the EO chain. In comparison to a terminal OH group, a terminal methyl group reduces water solubility, which results in a higher concentration of the surfactant at the air/water interface vs. bulk solution. This likely leads to a lower surface tension at concentrations at or above the CMC.

These results do not mean that methyl ester ethoxylates are better or worse than alcohol ethoxylates; it just means that they are different. Results do suggest, however, that methyl ester ethoxylates are quite surface-active, in the range of alcohol ethoxylates, and should perform well in terms of detergency performance, hard-surface cleaning, etc. Methyl ester ethoxylates, however, like alcohol ethoxylates, require optimization of both the alkyl carbon chainlength and the EO content to achieve optimal surface properties as well as optimal performance.

Foaming. The ability to generate foam was measured with a Schlag foam generation apparatus (11). Results (Fig. 10) show that methyl ester ethoxylates produce less foam than their alcohol ethoxylate counterparts. This is presumably due to the fact that methyl ester ethoxylates are sterically more bulky due to the presence of the ester carbonyl group, and the absence of a terminal hydroxyl group on the EO chain. Methyl ester ethoxylates, however, should be considered moderate to low foamers, like their alcohol ethoxylate counterparts.

Visually, the foam quality and foam stability properties of methyl ester ethoxylates appear to be identical with those of their alcohol ethoxylate counterparts.

Color/clarity/odor. Evaluation of color, clarity, and odor was done subjectively.

Differences in aesthetics between methyl ester and alcohol ethoxylates appear to be dependent on the ethoxylation feedstocks. With respect to lauryl-range ethoxylates, both methyl ester ethoxylates and alcohol ethoxylates are clear; the methyl ester ethoxylate, however, appears to have an overall lower level of odor. This appears to be related to the lower volatility of unethoxylated methyl ester in comparison to unethoxylated lauryl alcohol.

The tallow methyl ester ethoxylates had a slight yellow tint, related to a corresponding yellow tint in the starting material. In terms of odor, the methyl ester ethoxylate had a slightly higher level of odor in comparison to the tallow alcohol ethoxylate.

Performance properties. (i) detergency performance. Detergency performance was measured by using the protocol, test conditions, and formulation described in Table 4. As shown in Figure 11, methyl ester ethoxylates perform similarly to their alcohol ethoxylate counterparts. Although minor differences in detergency performance are observed, these differences are likely due to the fact that surfactant composition has not been optimized for the test conditions used; they are not due to an inherent difference in detergency performance between the surfactant types. It is clear, however, that

TABLE 5
Hydrolytic Stability Measurements of 10% Aqueous Solutions of Tetradecyl Methyl Ester 60% Ethoxylate at pH = 7 and 9 at 40°C

	pH 7 Study		pH 9 Study	
Buffer	KH_2PO_4/K_2HPO_4 (0.05 M each)		$Na_2B_4O_7$ (0.01 m)	
Initial pH	6.8		8.9	
Final pH	6.6		8.0	
	Storage time (d)	Percentage decomposition[a]	Storage time (d)	Percentage decomposition[a]
	0	0	0	0
	80	4	81	13.5

[a] Mol% saponified MeO(EO)$_n$H (as measured by ^{13}C nuclear magnetic resonance spectroscopy). See Table 1 for abbreviation.

TABLE 6
Melting Point Measurements (°C) of Methyl Ester and Alcohol Ethoxylates

Ethoxylate description	Melting point range (°C)
Lauryl-65% methyl ester ethoxylate	17.8–19.1
Lauryl-65% alcohol ethoxylate	17.8–19.1
Tallow-65% methyl ester ethoxylate	32.7–34.0
Tallow-65% alcohol ethoxylate	38.1–39.7

methyl ester ethoxylates can provide detergency comparable to that of alcohol ethoxylates.

The impact of EO chainlength on detergency is shown in Figure 12. Optimal EO content appears to depend on soil/cloth-type, just like that of alcohol ethoxylates. Optimal EO content clearly depends on targeted performance criteria.

(ii) Hard-surface cleaning performance. Hard-surface cleaning performance was tested with a Gartner straight-line washability and abrasion machine that was modified to improve reproducibility and permit simultaneous testing of three different test cleaning solutions. Equipment and protocol are described elsewhere (12). Graphite soil on latex paint, and wax soil on latex paint were used as test soil-substrates.

Previous studies have shown that optimal hard-surface cleaning performance for alcohol ethoxylates is achieved with a shorter (C_6–C_{10}) hydrophobe chainlength (12,13). This enhancement in performance is believed to result from an increase in the ability of the surfactant to act as a solvent to assist in soil removal.

Hard-surface cleaning results are shown in Table 9 and Figures 13 and 14. As shown, trends observed with alcohol ethoxylates are also observed with methyl ester ethoxylates. Hard-surface cleaning performance is observed to increase with both decreasing carbon chainlength of the hydrophobe, and with a lower level of ethoxylation. Results also suggest that methyl ester ethoxylates are even better suited for hard-surface cleaning applications in comparison to alcohol ethoxylates, based on the fact that octyl-60% methyl ester ethoxylate outperformed our high-performance standard, a $C_{6–10}$ 50% conventional alcohol ethoxylate.

(iii) Dishwashing performance. The performance of methyl ester ethoxylates in dishwashing formulations was not examined because ethoxylates are typically used as minor components in anionic-based formulations. Use of methyl ester ethoxylates in such mixed surfactant systems is currently under examination.

Environmental/human safety. The biodegradability of lauryl-range methyl ester ethoxylates was evaluated by using the SCAS biodegradation test (14,15). All methyl ester ethoxylates tested underwent complete removal (100% dissolved organic carbon loss) in the SCAS test. SCAS data further suggest that, even in water receiving poorly treated or raw wastewater, methyl ester ethoxylates should eventually be mineralized to CO_2 and water. Because more than 70% dissolved organic carbon removal occurred in the SCAS test, the Organization for Economic Cooperation and Development would define methyl ester ethoxylates as being “inherently biodegradable” and conclude that they are susceptible to ultimate mineralization in the environment.

Rabbit skin irritation tests were performed on lauryl-range 60% methyl ester ethoxylate vs. a conventional lauryl-range alcohol ethoxylate. The methyl ester ethoxylate had a primary irritation index of 0.9 (on a scale of 0 to 8), in comparison to 1.9 for the conventional ethoxylate. An index of 0.9 is described as “slightly irritating,” while an index of 1.9 is on the

TABLE 7
Viscosity (cps)[a] of Methyl Ester vs. Alcohol Ethoxylates

	100% Ethoxylate		30% Aqueous solution		15% Aqueous solution
	40°C	50°C	25°C	40°C	25°C
Lauryl-65% methyl ester ethoxylate	54	61	27	30	22
Lauryl-65% alcohol ethoxylate	49	38	32	25	13
Tallow-65% methyl ester ethoxylate	116	62	926	1100	20
Tallow-65% alcohol ethoxylate	64	52	gel	44	20

[a] Brookfield Digital Viscometer (Model DV-II) (Stoughton, MA); spindle 41; shear setting = 5.0 (shear rate = 2.5 s^{-1}).

TABLE 8
Water Solubility Measurements (inverse cloud points: °C)[a] of Methyl Ester Ethoxylates and Alcohol Ethoxylates

Ethoxylate description	Inverse cloud point (°C)
Lauryl-55% methyl ester ethoxylate	38
Lauryl-60% methyl ester ethoxylate	49
Lauryl-65% methyl ester ethoxylate	63
Lauryl-70% methyl ester ethoxylate	75+
Lauryl-65% alcohol ethoxylate	81
Tallow-65% methyl ester ethoxylate	62
Tallow-65% alcohol ethoxylate	87

[a] Inverse cloud point is determined by heating 1% aqueous solutions and determining the temperature at which the solution clouds; the higher the inverse cloud point, the greater the water solubility.

TABLE 9
Hard-Surface Cleaning Performance

	Cleaning index[a] ± SD	
Ethoxylate description	Graphite soil	Wax soil
Lauryl-55% methyl ester ethoxylate	5.1 ± 0.4	0.4 ± 0.0
Lauryl-60% methyl ester ethoxylate	2.8 ± 0.0	0.3 ± 0.1
Lauryl-65% methyl ester ethoxylate	2.6 ± 0.2	0.1 ± 0.0
Octyl-60% methyl ester ethoxylate	12.5 ± 01	2.0 ± 0.0
Tallow-60% methyl ester ethoxylate	4.3 ± 0.1	0.0 ± 0.0
Std.-nonylphenol-9-mol ethoxylate	6.6 ± 0.9	0.1 ± 0.0
Std.-$C_{6–10}$-50% alcohol ethoxylate	10.7 ± 0.8	1.7 ± 0.2

[a] Cleaning index = (reflectance of cleaned substrate) – (reflectance of soiled substrate)/number of test strokes.

borderline with “moderately irritating.” These results suggest that methyl ester ethoxylates may have an inherent advantage in terms of mildness.

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