

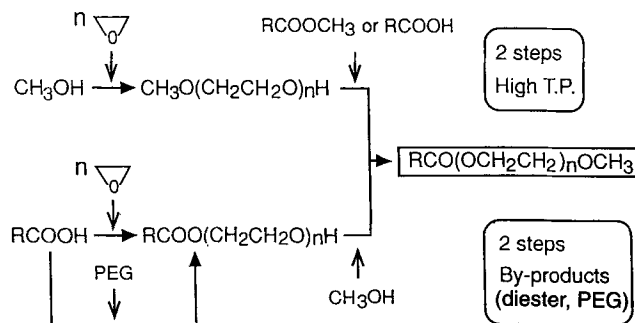
Preparation and Properties of Ethoxylated Fatty Methyl Ester Nonionics¹

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ABSTRACT: Ethylene oxide (EO) cannot react directly with fatty methyl esters that have no active hydrogen. We developed a new synthetic method, which directly inserts EO into fatty methyl esters (RCOOCH₃) to give [RCO(OCH₂CH₂)_nOCH₃]. This was achieved by the use of a novel solid catalyst modified by metal cations. Ethoxylates of fatty methyl esters obtained by this method were homogeneous monoesters and had good properties as nonionic surfactants. *JAOCS* 72, 781–784 (1995).

KEY WORDS: Acid–base bifunctional catalyst, coordination anionic polymerization, detergency, ethoxylated fatty methyl ester, ethoxylation, ethylene oxide, fatty methyl ester, foam, hydrolysis, magnesium oxide, nonionic surfactant, phase diagram, solid catalyst.



Ethoxylated fatty acid esters are well known as ether–ester-type nonionic surfactants. For example, ethoxylated stearyl stearates are used as emulsifiers, dispersants, or oil phase adjusters in cosmetics or in industrial products (1). The ethoxylated methyl laurates have been studied as wetting agents (2).

Alcohol ethoxylates and fatty acid ethoxylates, which are typical ethylene oxide (EO)-based nonionic surfactants, can be readily obtained (3) by the direct reaction of fatty alcohols or fatty acids that have an active hydrogen in their molecules with EO in the presence of an alkali[±] (e.g., sodium hydroxide) or an acidic catalyst (e.g., antimony pentachloride). EO, however, cannot directly react with fatty methyl esters that have no active hydrogen by using those catalysts. Strictly speaking, although this reaction proceeds slightly, its reaction activity and selectivity are too poor for industrial applications.

As Scheme 1 indicates, there are two conventional methods for synthesizing ethoxylated fatty methyl esters (EFMe). One method is to synthesize EFMe through methyl glycol ethers from methanol. The other way is to synthesize EFMe through fatty acid ethoxylates from fatty acids. In either case, practical applications are difficult to achieve, due to a trou-

blesome two-step reaction at high temperature/pressure and the by-products, such as diesters and polyethylene glycol. If a new synthetic method for the direct insertion of EO into fatty methyl esters were developed, EFMe nonionic surfactants could be easily obtained from natural fats and oils.

In this work, a new method to produce EFMe with a novel solid catalyst will be described. The properties of EFMe thus obtained are also described.

EXPERIMENTAL PROCEDURES

Reaction procedures. Methyl laurate (Paster M12, Lion Corp., Tokyo, Japan) and catalysts were charged in a stirred stainless-steel autoclave, and air inside the autoclave was displaced with nitrogen. The mixture was heated to 180°C under stirring. EO (Mitsubishi Petrochemical, Tokyo, Japan) was supplied to the autoclave, and the atmosphere in the autoclave was maintained at a temperature of 180°C and a pressure of 3 atm. The feed of EO was stopped when the desired amount of EO was supplied. After aging, the reaction mixture was cooled, and the catalyst was filtered out from it.

Analytical procedures. The purity of the reaction products was ascertained by ¹H nuclear magnetic resonance (NMR), high-performance liquid chromatography (HPLC) and gas chromatography techniques.

The EO adduct distributions of EFMe were determined with an HPLC (Shimadzu LC-6A; Shimadzu, Kyoto, Japan) with an ultraviolet (UV) detector (Shimadzu SPD-10A) and a Zorbax C8 column (DuPont, Boston, MA). A 60% acetonitrile–water mixture was used as a mobile phase.

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TABLE 1
Experimental Methods for Measuring Properties

Determination	Procedure
Critical micelle concentration	Wilhelmy method
Surface tension	Wilhelmy method
Wettability	Draves method
Solubilization	Solubility of Yellow OB
Foaming	Ross-Miles method
Detergency performance	Terg-O-Tometer
Hydrolysis	HPLC method ^a

^aHigh-performance liquid chromatography (HPLC) method: HPLC, Shimadzu LC-6A (Shimadzu, Kyoto, Japan); RI detector, Shimadzu RID-6A; column, Nucleosil 5SB (4.6 × 250 mm) (Macherey-Nagel, Düren, Germany); mobile phase, 0.25 wt% NaClO₄-CH₃OH/H₂O (80:20).

Measurement of properties. The properties of the reaction products were measured by the methods shown in Table 1. Details are included in the Results and Discussion section.

RESULTS AND DISCUSSION

Direct insertion of EO into fatty methyl esters. As mentioned previously, many kinds of alkaline or acidic catalysts have been proposed for the ethoxylation of fatty alcohols or fatty acids. Recently, some novel catalysts were studied to obtain narrow-range ethoxylate with a narrow EO distribution (4–7). Catalysts suitable for the ethoxylation of fatty alcohols were applied for the purpose of ethoxylation of fatty methyl esters.

In Tables 2 and 3, only magnesium oxide catalysts, modified by metal cations, demonstrated sufficient reactivity to achieve the direct insertion of EO into fatty methyl esters that had no active hydrogen.

TABLE 2
Synthesis of Ethoxylates of Fatty Methyl Esters by the Reaction of Methyl Laurate with Ethylene Oxide (EO) over Various Basic or Acidic Catalysts^a

Catalyst	Reaction temperature (°C)	Catalyst concentration (wt%/FAME)	Reaction rate (g EO/min/g catalyst)		
NaOH	180	0.1	Negligible		
KOH	↓	↓	Negligible		
NaOCH ₃			Negligible		
NaOC ₂ H ₅			Negligible		
MgO			1.0	No reaction	
CaO			↓	No reaction	
SrO	↓	↓	No reaction		
BaO			No reaction		
H ₂ SO ₄			80	0.5	No reaction
H ₃ PO ₄			No reaction		
BF ₃			No reaction		
SnCl ₄			No reaction		
SbCl ₅			No reaction		
AlCl ₃			No reaction		

^aFAME, Methyl laurate.

TABLE 3
Synthesis of Ethoxylates of Fatty Methyl Esters by the Reaction of Methyl Laurate with Ethylene Oxide (EO) over Bifunctional Catalysts^a

Catalyst	Reaction temperature (°C)	Catalyst concentration (wt%/FAME)	Reaction rate (g EO/min/g catalyst)
Al-MgO	↓	↓	0.92
Ga-MgO			0.39
In-MgO			0.03
Sc-MgO			0.01
Cr-MgO			0.01
Mn-MgO			0.11
Fe-MgO			No reaction
Co-MgO			0.01
Ni-MgO			No reaction
La-MgO			0.03
Al-CaO			No reaction
Fe-CaO			No reaction
Al-SrO			No reaction
Fe-SrO			No reaction
Al-BaO			No reaction
Fe-BaO	No reaction		

^aSee Table 2 for abbreviation.



Figure 1 shows a ¹H NMR spectrum of the reaction product, which was catalyzed by magnesium oxide modified by metal cation. By the chemical shifts and signals' strengths, it was confirmed that EO was directly inserted between the acyl group and the methoxy group of the methyl esters. We believe that this reaction proceeded by coordination anionic polymerization. Although there is no definite evidence for the reaction mechanism, the species indicated in Scheme 2 can be considered to be formed by a dissociative chemisorption on the active site of the catalyst's surface.

By-products and decomposed substances were not detected (Table 4). The amount of unreacted fatty methyl ester depends on an average EO adduct number, and it decreases with increasing EO adduct number. Figure 2 shows an example of the EO adduct distribution of EFME. It was confirmed

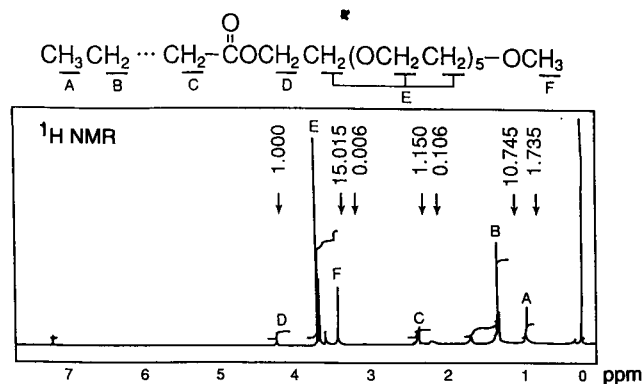
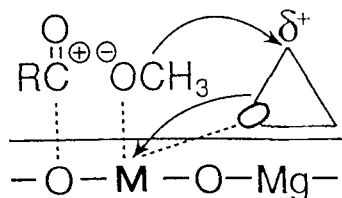


FIG. 1. ¹H Nuclear magnetic resonance (NMR) spectrum of the reaction product (C12 • Me-6EO:EFME).



SCHEME 2

TABLE 4
Analysis of Ingredient of the Reaction Product (C12 • Me-nEO:EFMe)^a

Average EO adduct number	6	10	15
C ₁₁ H ₂₃ CO(EO) _n OCH ₃ (wt%)	97.5	100	100
C ₁₁ H ₂₃ COOCH ₃ (wt%)	2.5	0	0
Polyethylene glycol	Not detected	Not detected	Not detected
C ₁₁ H ₂₃ COOH	Not detected	Not detected	Not detected
C ₁₁ H ₂₃ COO(EO) _n H	Not detected	Not detected	Not detected
CH ₃ OH	Not detected	Not detected	Not detected
CH ₃ O(EO) _n H	Not detected	Not detected	Not detected
Color [APHA]	10	10	10

^aEFMe, ethoxylated fatty methyl ester; EO, ethylene oxide; APHA, American Public Health Association Method (Ref. 8).

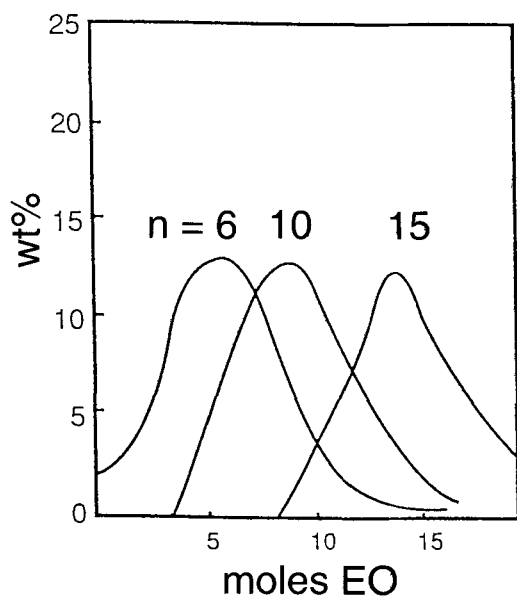


FIG. 2. Ethylene oxide (EO) distribution of C12 • Me-nEO(EFMe). Abbreviations as in Figure 1.

that EFMe obtained by the new synthetic method were almost homogeneous monoesters.

Properties of EFMe as nonionics. Table 5 shows the characteristics of EFMe in a comparison of ethoxylated methyl laurate (C12 • Me-nEO:EFMe) with ethoxylated lauryl alcohol with a conventional EO adduct distribution [C12 • OH-6EO:BRE (BRE, alcohol ethoxylate nonionics)].

Critical micelle concentration, surface tension, and the wettability of EFMe were almost the same as for BRE. EFMe

TABLE 5
Characteristics of EFMe^a

	EFMe			BRE
	Methyl laurate	Lauryl alcohol		
Average EO adduct number	6	10	15	6
Hydrophile-lipophile balance	11	13	15	11
Critical micelle concentration (CMC) 25°C (wt%)	10 ⁻²	10 ⁻²	10 ⁻²	10 ⁻²
Surface tension: γ CMC (dyne/cm) 25°C	30	31	32	35
Wettability (s) 0.1 wt%, 25°C	9	10	14	10
Solubilization (ppm) 0.1 wt%, 25°C	21	17	12	6
Foaming (mm) 0.1 wt%, 25°C	initial	40	63	79
	5 min	16	25	50

^aAbbreviations as in Table 4; BRE, conventional alcohol ethoxylate.

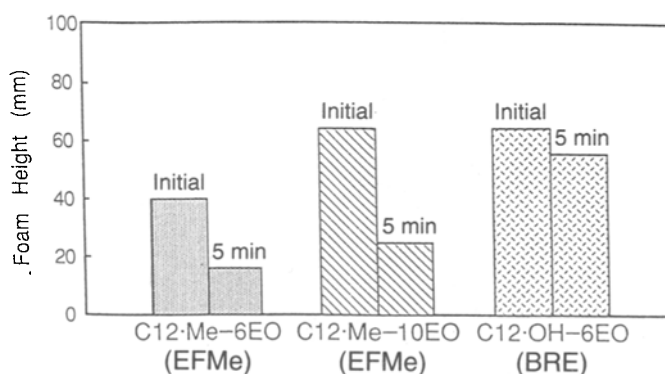


FIG. 3. Foaming performance of EFMe; Ross-Miles method, condition; 0.1 wt% aqueous solution; BRE, alcohol ethoxylate. Abbreviations as in Figure 1.

had a high solubilization of Yellow OB and an interesting foaming performance.

Figure 3 shows foaming performance of EFMe as measured by the Ross-Miles method. For the same average EO adduct number, e.g., 6EO, the initial foam height of EFMe was relatively low compared with that of BRE. For the same initial foam height, the foam height of EFMe after 5 min was low, showing that the foam of EFMe can disappear quickly. This foaming performance of EFMe may be applicable to detergents to produce a good rinsing performance.

Figure 4 shows the phase diagrams of C12 • Me-15EO (EFMe) and C12 • OH-15EO (BRE) (9). Although alcohol ethoxylate had a large hexagonal or cubic liquid-crystal phase, EFMe had only a small hexagonal phase. In other words, the gelling range of the EFMe aqueous solution was small.

Figure 5 shows the detergency of EFMe compared with other surfactants. EFMe had good detergency, which was equivalent to that of BRE and other anionic surfactants.

Figure 6 shows the hydrolysis of EFMe under differing pH conditions. EFMe has an ester-bonding, and, consequently, in

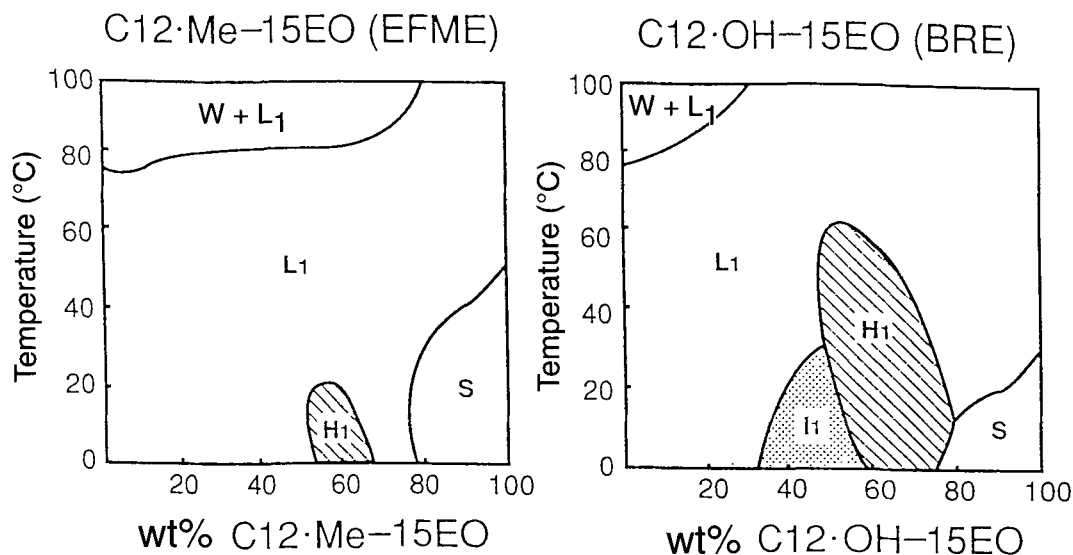


FIG. 4. Phase diagrams of EFMe/water systems. L₁, micellar solution; I₁, cubic phase of closed-packed spherical micelles; H₁, normal hexagonal phase; S, hydrated solid; W, dilute surfactant solution. Abbreviations as in Figures 1 and 3.

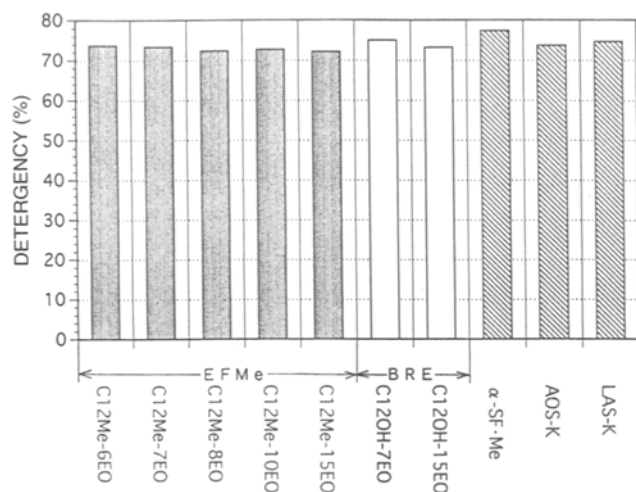


FIG. 5. Detergency of EFMe compared with other surfactants. Terg-O-Tometer, conditions: surfactant, 350 ppm; zeolite, 170 ppm; Na₂CO₃, 200 ppm; 3°DH, 25°C; AOS, α-olefin sulfonate; LAS, linear alkyl benzene sulfonate. Other abbreviations as in Figures 1 and 3.

the strongly alkaline range, it was hydrolyzed. In the wide neutral range, however, it was stable.

Judging from this, EFMe could be used as a nonionic surfactant with typical foaming performance, good aqueous solution properties, and high detergency.

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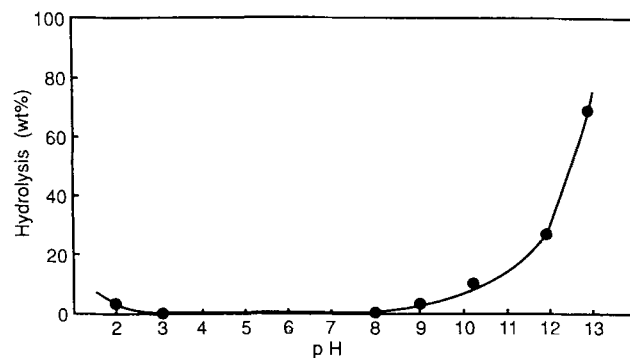


FIG. 6. Hydrolysis of C12 • Me-15EO (EFMe). Conditions: 1 wt%, 60°C, 24 h.

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