# Effects of Ethoxylate Structure on Surfactant Properties of Ethoxylated Fatty Methyl Esters

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**ABSTRACT:** In the presence of a surface-modified Al–Mg composite oxide catalyst, ethoxylated fatty methyl esters with different hydrophobic group structures and different chainlengths of polyoxyethylene were synthesized from fatty methyl esters by direct ethoxylation. Each ethoxylated fatty methyl ester obtained showed a narrow ethylene oxide (EO) adduct distribution. Foaming, ability to lower surface tension, ability to lower interfacial tension, wettability, and dye solubilization were measured. Ethoxylated methyl laurate with about 60 to 70% EO content was found to be the most suitable as a base surfactant for household detergents.

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**KEY WORDS:** Direct ethoxylation, ethoxylated fatty methyl ester, ethylene oxide, fatty methyl ester, foaming, interfacial tension, nonionic surfactant, solubilization, surface tension, wettability.

The synthesis of an ethoxylated fatty methyl ester (EFME) by the direct ethoxylation of a fatty methyl ester has been reported recently (1–7). In a previous paper, we reported that this reaction proceeded easily in the presence of an Al–Mg composite catalyst with or without surface modification (1,2). The EFME products made in this manner are almost 100% homogeneous in monoester and show good surface-active properties, such as ability to lower surface tension, wettability, and solubilization. They are anticipated to be new ester-ether type nonionic surfactants that can be favorably utilized in the detergent industry (1,4,5,8).

In this report, we will discuss how and to what degree the structure of hydrophobic groups and polyoxyethylene (POE) chainlength of the EFME influence surfactant properties.

## EXPERIMENTAL PROCEDURES

*Materials.* In the presence of a surface-modified Al–Mg composite oxide catalyst, EFME with a narrow ethylene oxide (EO) adduct distribution were synthesized from fatty acid methyl esters (FAME) of various alkyl chainlengths (Paster series; Lion Corp., Tokyo, Japan) and EO (Mitsubishi Chemical, Tokyo, Japan) by the method of Hama *et al.* (9). The combinations of FAME alkyl chainlength and average POE chainlength used for the property evaluations are shown in Table 1.

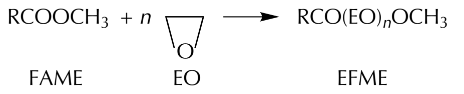
*Analysis for EO adduct distribution.* The EO adduct distributions of EFME were measured by liquid chromatography under the following conditions: column, Zorbax $C_8$ (4.6 mm × 250 mm; DuPont, Boston, MA); mobil phase, $CH_3CN/H_2O$ = 60:40; ultraviolet detector (SPD-10A; Shimadzu, Kyoto, Japan); measuring wavelength, 220 nm.

Examples of EO adduct distributions of the ethoxylated methyl laurate ($C_{12}$-EFME) with different EO chainlengths are shown in Figure 1A. Examples of EFME with 9 moles of EO and different alkyl chainlengths are shown in Figure 1B.

*Cloud point.* Aqueous cloud points were measured visually at surfactant concentrations of 1%.

*Foaming and foam stability.* Foaming and foam stability of 1% aqueous solutions of each sample were measured by the Ross-Miles Method at 25°C (10). Foam stability was calculated based on the change of the foam heights from soon after dropping the sample solution ($t$ = 0) to 5 min after dropping ($t$ = 5) (11).

**TABLE 1**
**Evaluation Samples**[a]



| FAME | Average EO adduct number: POE ($n$) 6 | 8 | 9 | 12 | 15 |
|---|---|---|---|---|---|
| $C_8$Me/methyl caprylate | ○ | | ○ | | ○ |
| $C_{10}$Me/methyl caprate | ○ | | ○ | | ○ |
| $C_{12}$Me/methyl laurate | ○ | ○ | ○ | ○ | |
| $C_{14}$Me/methyl myristate | ○ | | ○ | | ○ |
| $C_{16}$Me/methyl palmitate | ○ | | ○ | | ○ |
| $C_{18:0}$Me/methyl stearate | | | ○ | | |
| $C_{18:1}$ Me/methyl oleate | ○ | | ○ | | ○ |

[a] FAME, fatty acid methyl ester; EO, ethylene oxide; POE, polyoxyethylene; EFME, ethoxylated fatty methyl ester.

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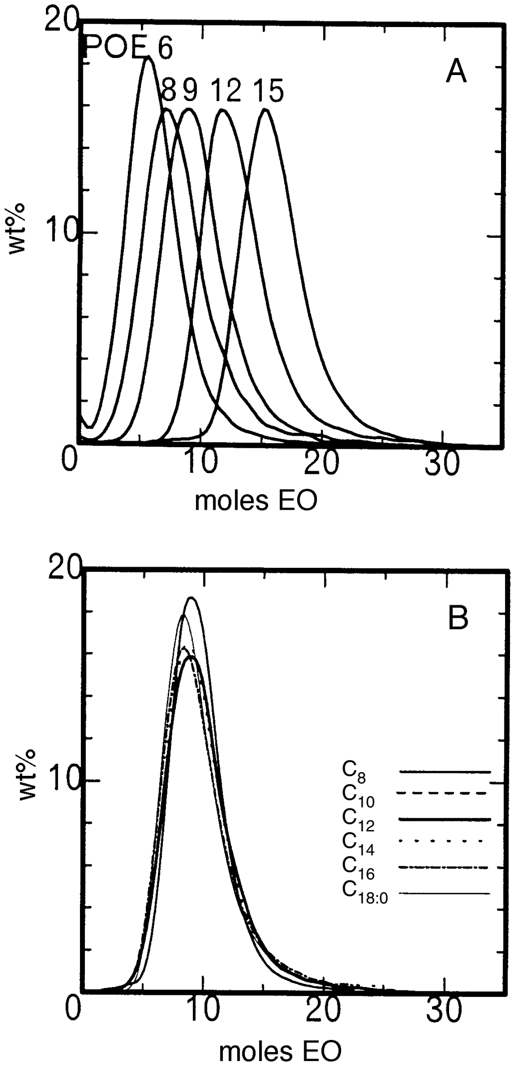

**FIG. 1.** Ethylene oxide (EO) adduct distribution of ethoxylated fatty methyl ester (EFME): A: $C_{12}$-EFME; B: $RCO(EO)_9OCH_3$; POE, polyoxyethylene.

*Ability to lower surface tension.* Aqueous surface tension lowering was measured by the Wilhelmy plate method at 25°C. Critical micelle concentrations (CMC), surface tensions at the CMC ($\gamma_{CMC}$), and areas per molecule at the interface ($A_{CMC}$) were calculated.

*Interfacial tension lowering.* Interfacial tensions (0.1% aqueous) against *n*-decane (Tokyo Kasei, Tokyo, Japan), oleic acid (Kanto Chemicals, Tokyo, Japan), and triolein (Kanto Chemicals) were measured by the Wilhelmy method.

*Wettability.* The wetting times of 0.1% aqueous surfactant solutions were measured by the Draves method at 25°C. Test cloth of 100% wool felt (3 × 20 cm) (Japan Wool Textile, Osaka, Japan) was used.

*Solubilization.* Solubilization of Yellow OB dye by 0.1% aqueous surfactant solutions was measured at 25°C.

## RESULTS AND DISCUSSION

*Cloud point.* Figure 2 shows a plot of cloud point vs. average EO number for each EFME sample. When the EO content (in moles) is held constant, cloud points tend to drop with the increase of the FAME alkyl chainlength. However, when the average POE is 15 or more, the cloud points tend to converge regardless of the alkyl chainlength.

*Foaming.* Initial foam heights of EFME vs. the average EO number are shown in Figure 3. Maximum foaming occurs around POE 12 for the $C_{12}$-EFME. Foam stability as a function of EO number is shown in Figure 4. $C_8$- and $C_{10}$-EFME show lower values of foam stability (faster breaking).

*CMC and ability to lower surface tension.* Figure 5 shows CMC values for each EFME as a function of EO number. CMC decreases as the alkyl chainlength becomes longer. The effect of EO chainlength on the CMC is small. $\gamma_{CMC}$ increases with EO chainlength (Fig. 6), but the effect of alkyl chainlength is small. The area per molecule at the air–liquid interface was calculated from surface tension measurement data (12) and is shown in Figure 7 as a function of EO number. The area per molecule increases with decreasing alkyl chainlength. The area per molecule also increases with an increase in EO chainlength, with the exception of $C_{18:1}$ (oleate).

*Ability to lower interfacial tension.* Interfacial tensions between 0.1% aqueous solutions of EFME and three kinds of oils (*n*-decane, oleic acid, triolein) were measured and plotted against EO number (Fig. 8). $C_{10}$- to $C_{14}$-EFME are

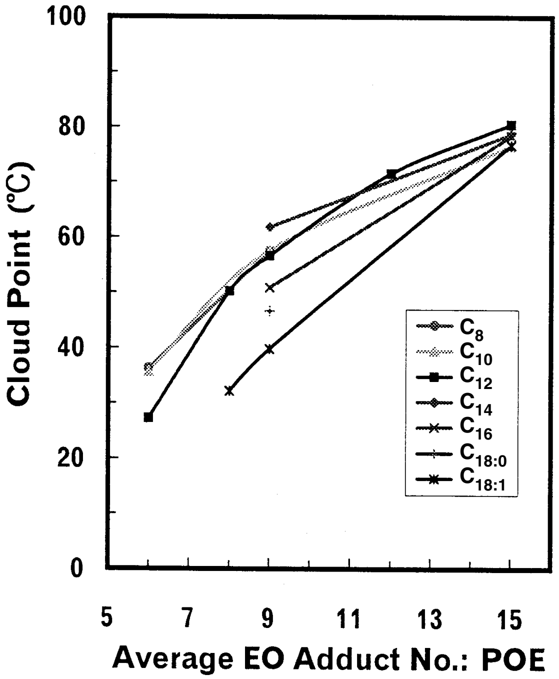

**FIG. 2.** Cloud point of EFME as a function of average EO number. See Figure 1 for abbreviations.

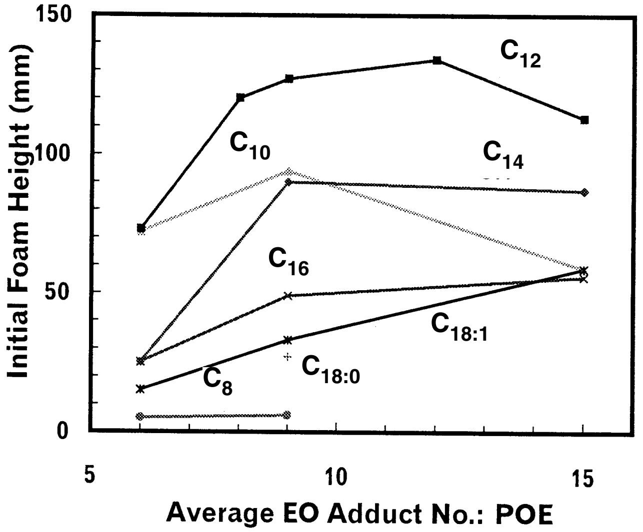

**FIG. 3.** Foaming of EFME as a function of average EO number. See Figure 1 for abbreviations.

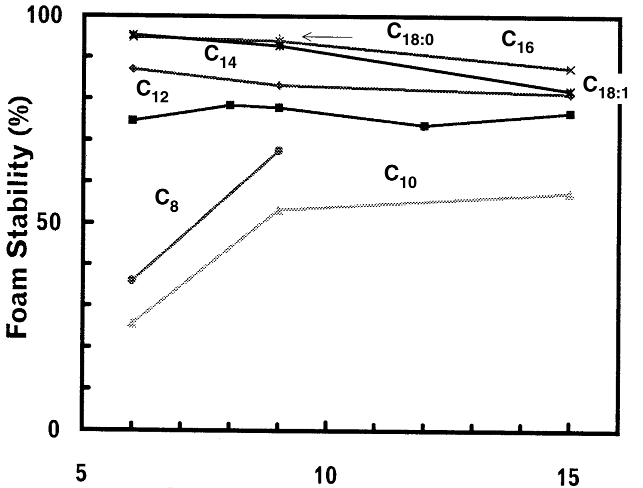

**FIG. 4.** Foam stability of EFME as a function of average EO number. See Figure 1 for abbreviations.

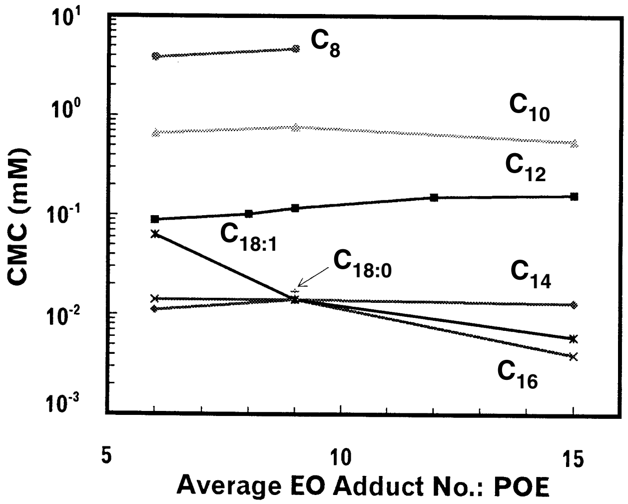

**FIG. 5.** Critical micelle concentration (CMC) of EFME as a function of average EO number. See Figure 1 for abbreviations.

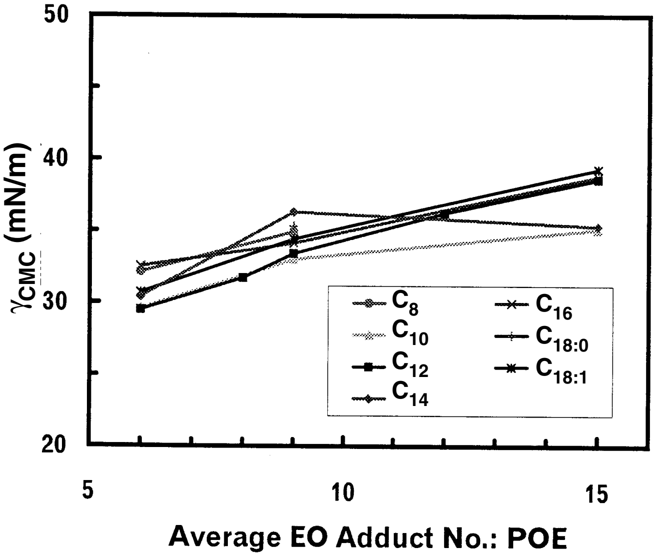

**FIG. 6.** Areas per molecule at the interface of EFME as a function of average EO number. See Figures 1 and 5 for abbreviations.

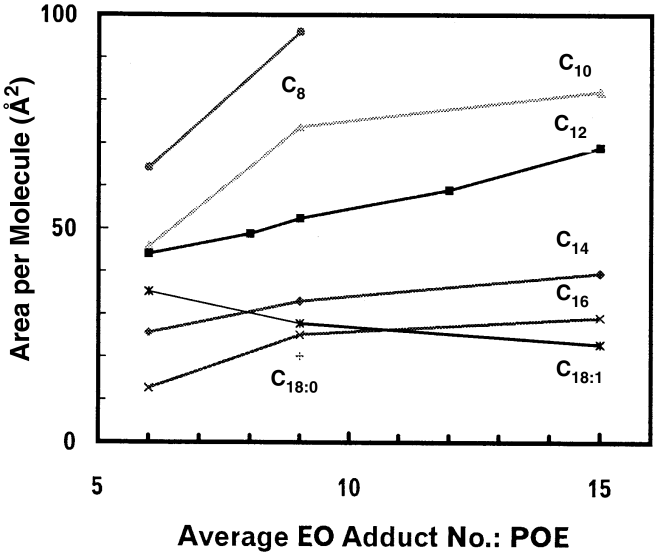

**FIG. 7.** Area per molecule of EFME as a function of average EO number. See Figures 1 and 2 for abbreviations.

superior in their ability to lower interfacial tension against *n*-decane. For oleic acid, all materials behaved similarly. For triolein, the overall trend is similar. That is, $C_{10}$- to $C_{14}$-EFME with long EO chainlengths are superior in interfacial tension lowering.

*Wettability*. Wetting times for EFME vs. EO number are shown in Figure 9. $C_{10}$- to $C_{14}$-EFME show favorable wettability. Among them, $C_{12}$-EFME shows the best wettability (lowest wetting times).

*Solubilization*. As shown in Figure 10, dye solubilization occurred when the alkyl chainlength was $C_{12}$ or more but was not observed at all in the $C_8$- and $C_{10}$-EFME systems. A reason for this behavior is that the number of micelles present at

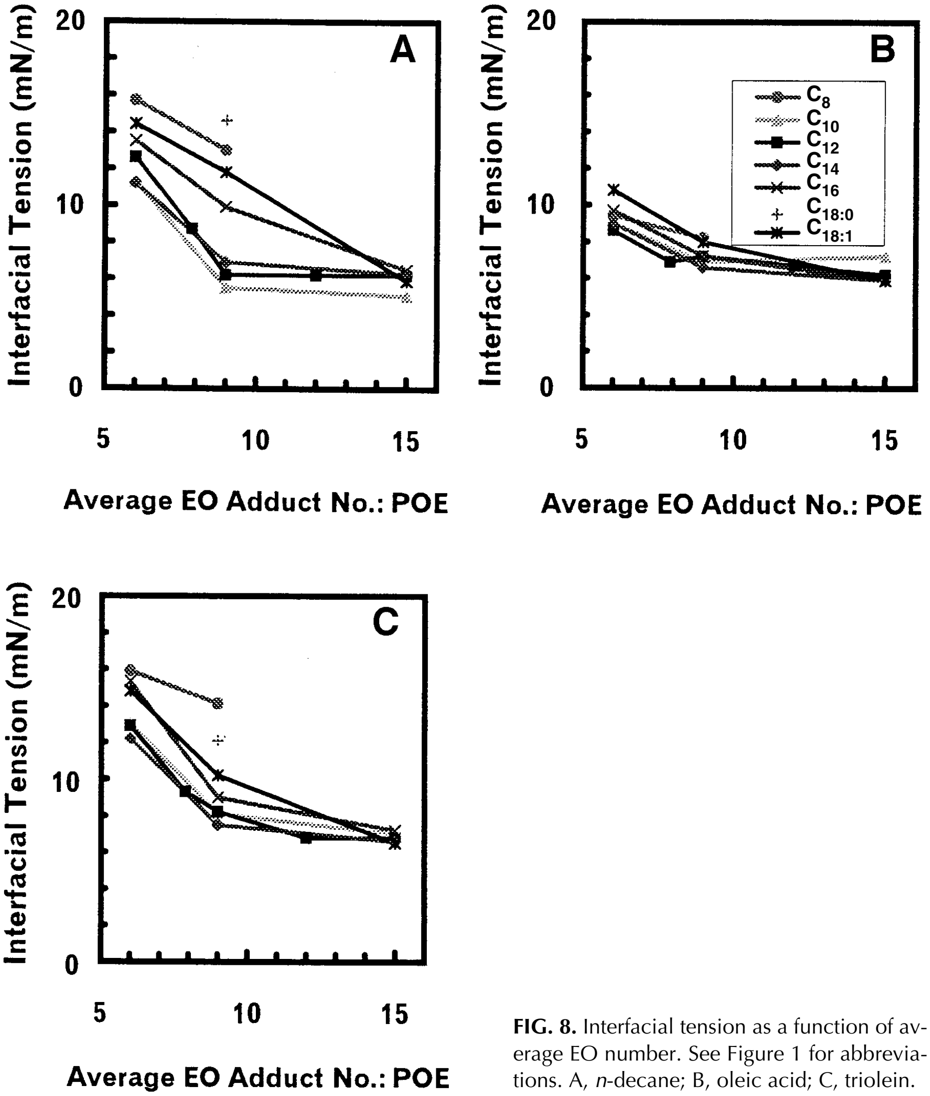

**FIG. 8.** Interfacial tension as a function of average EO number. See Figure 1 for abbreviations. A, *n*-decane; B, oleic acid; C, triolein.

the 0.1% measurement concentration is extremely small due to the high CMC of $C_8$- and $C_{10}$-EFME. The EFME of alkyl chainlength $C_{12}$ or higher show increased solubilization of Yellow OB as the alkyl chainlength increases and the EO

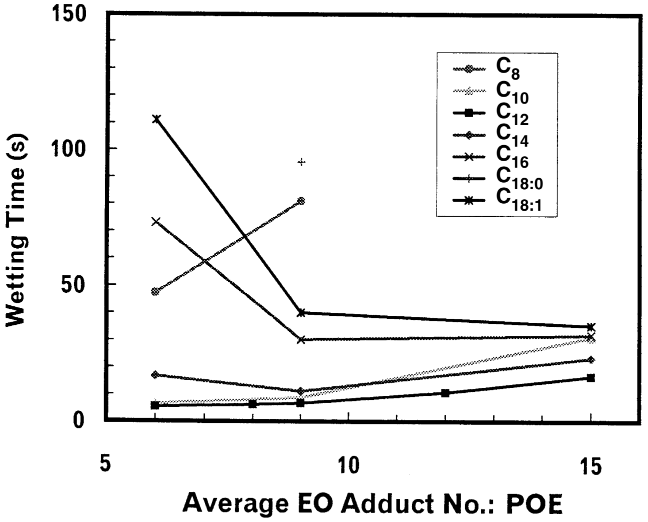

**FIG. 9.** Wettability of EFME as a function of average EO number. See Figure 1 for abbreviations.

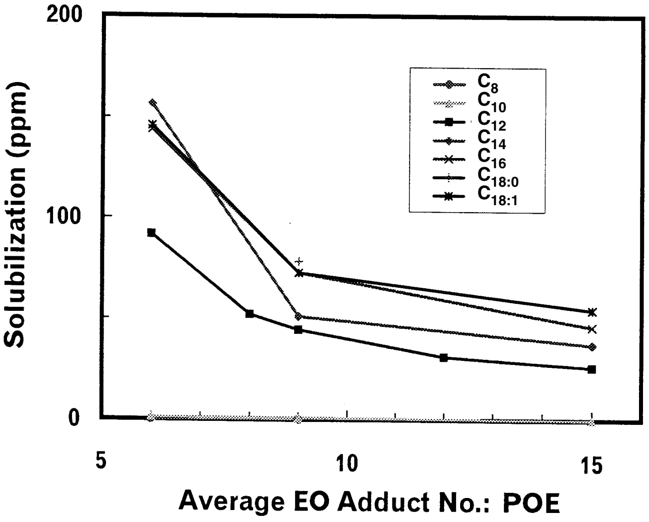

**FIG. 10.** Dye solubilization of EFME as a function of average EO number. See Figure 1 for abbreviations.

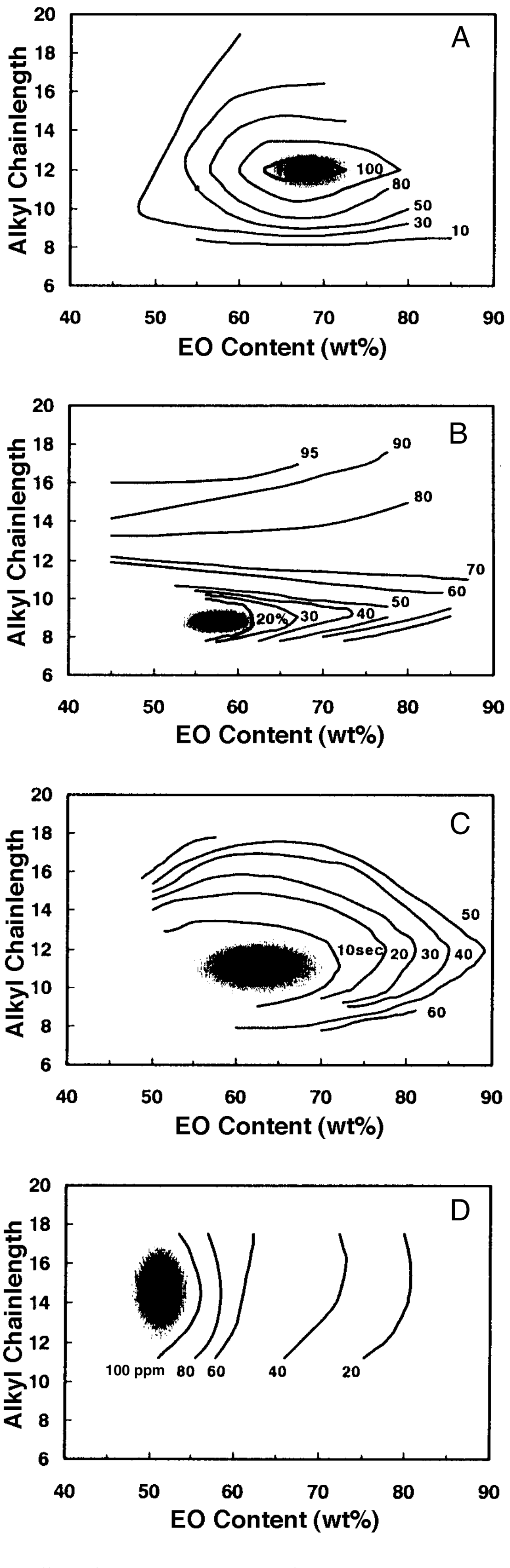

**FIG. 11.** Effect of EFME structure on surfactant properties. See Figure 1 for abbreviation; A, foaming; B, foam stability (foam breaking); C, wettability; D, solubilization.

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