Nonionic Surfactant Properties of Methoxypolyoxyethylene Dodecanoate Compared with Polyoxyethylene Dodecylether

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ABSTRACT: Nonionic surfactant properties of methoxypolyoxyethylene dodecanoate [C_{12}-EFME; $C_{11}H_{23}CO(OCH_2CH_2)_nCH_3$] with varying ethylene oxide (EO) adduct distributions were compared with those of polyoxyethylene dodecylether [C_{12}-alcohol ethoxylate (AE); $C_{12}H_{25}O(CH_2CH_2O)_nH$]. The gelling region of C_{12}-EFME was much smaller than that of C_{12}-AE due to the effects of the ester bond and the terminal methyl group. When the EO adduct distribution of EFME is narrowed, the cloud point and the ability to lower interfacial tension do not change appreciably. Other effects of narrow distribution on EFME performance include a decrease in the gellation region and better foam breaking and wetting.

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KEY WORDS: Alcohol ethoxylate, broad ethylene oxide adduct distribution, ethoxylated fatty methyl ester, ethylene oxide, foam breaking, foaming, gelling region, narrow ethylene oxide adduct distribution, phase diagram, wettability.

We have demonstrated that ethylene oxide (EO) can be directly inserted into fatty methyl ester by using Al-Mg composite oxide catalysts (1,2). The EO adduct distribution can be made narrower by modification of the catalyst (3). Moreover, we concluded that methoxypolyoxyethylene dodecanoate (C_{12}-EFME = ethoxylated fatty methyl ester) was most suitable as a detergent for household products. This conclusion was a result of detailed studies of surfactant properties related to the combination of alkyl chainlength and polyoxyethylene chainlength of various ethoxylated fatty methyl esters (4). Based upon the abovementioned results, this study clarifies the differences between EFME and alcohol ethoxylates (AE) by comparing surfactant properties of C_{12}-EFME with different EO adduct distribution (narrow C_{12}-EFME, broad C_{12}-EFME) and C_{12}-AE (C_{12}-NRE = narrow-range ethoxylate, C_{12}-BRE = broad-range ethoxylate).

EXPERIMENTAL PROCEDURES

Materials; EFME. C_{12}-EFME with narrow EO adduct distribution and broad C_{12}-EFME were synthesized from methyl dodecanoate (Paster M12; Lion Corp., Tokyo, Japan) and EO (Mitsubishi Chemicals, Tokyo, Japan) by the direct ethoxylation method described in our previous paper (3). Figure 1 shows EO adduct distribution of both EFME products as measured by high-performance liquid chromatography (HPLC) under the following conditions: Zorbax C8 column (4.6 mm × 250 mm; Du Pont, Boston, MA); eluent, CH_3CN/H_2O = 60:40; ultraviolet detector (SPD-10A; Shimadzu, Kyoto, Japan); wavelength, 220 nm.

AE. C_{12}-NRE with narrow EO adduct distribution was synthesized from Conol 20P (Shin-nihon Rika, Osaka, Japan) by the method of Nakamura *et al.* (5). A commercially available C_{12}-BRE with broad EO adduct distribution (EMALEX series, Nihon Emulsion, Tokyo, Japan) was used. Figure 2 shows the EO adduct distributions of NRE and BRE as measured under the following HPLC conditions: same column as for EFME; same eluent as for EFME; infrared detector (RID-6A; Shimadzu).

Table 1 shows all ethoxylate samples used for evaluation. In our previous paper (4), C_{12}-EFME with approximately 60

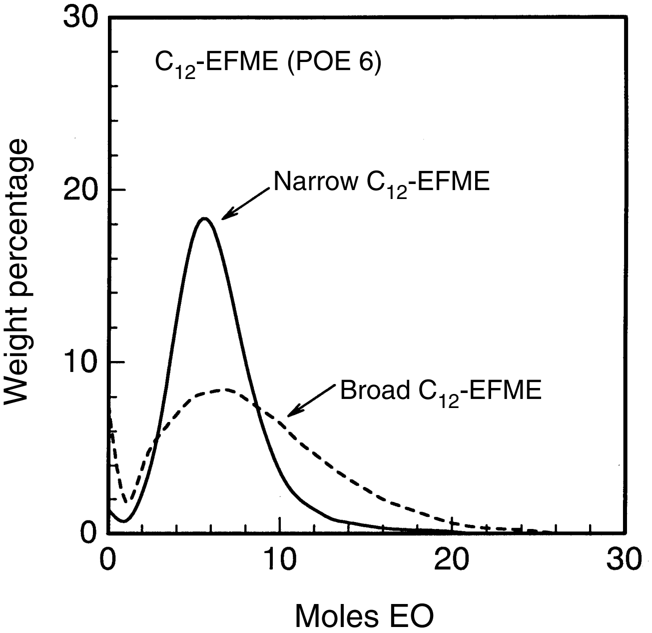

FIG. 1. Ethylene oxide (EO) adduct distributions of C_{12}-ethoxylated fatty methyl ester (EFME) (POE 6) samples.

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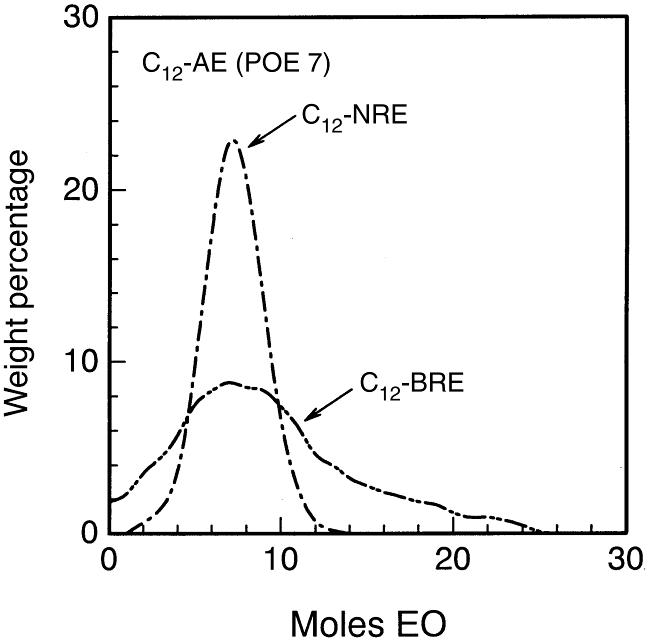

FIG. 2. EO adduct distributions of C_{12}-alcohol ethoxylate (AE) (POE 7) samples; BRE, broad-range ethoxylate; NRE, narrow-range ethoxylate. See Figure 1 for other abbreviation.

to 70 wt% EO (average EO adduct number 7 to 11) is most suitable for a base surfactant for household detergents. Therefore, we chose ethoxylates with 6 to 15 EO units (average) as samples for this study.

Cloud point. Cloud points of 1% aqueous solutions were measured.

Phase diagram. Phase diagrams were measured by the method described in our previous paper (6). Various compositions of surfactant and water were sealed in glass tubes. Each phase at the prescribed temperature was confirmed by using an optical microscope with crossed polarizers (Type 13H; Olympus Co. Ltd., Tokyo, Japan). The narrow C_{12}-EFME used here was obtained by distillation of broad C_{12}-EFME to give a product with about the same EO adduct distribution as the narrow C_{12}-EFME synthesized by the direct ethoxylation. Phase diagrams of narrow C_{12}-EFME (distillate) and broad C_{12}-EFME were compared to study the effect of EO adduct distribution. Then, a comparison between narrow C_{12}-EFME and C_{12}-NRE was made to study the difference between EFME and AE.

TABLE 1
Evaluated Samples[a]

	Average EO adduct number (POE)							
	6	7	8	9	10	11	12	15
Narrow C_{12}-EFME	○		○	○			○	○
Broad C_{12}-EFME	○		○			○		○
C_{12}-NRE		○		○			○	○
C_{12}-BRE		○		○	○		○	○

[a] EFME, ethoxylated fatty methyl ester; NRE, narrow-range ethoxylate; EO, ethylene oxide; POE, polyoxyethylene; BRE, broad-range ethoxylate.

Foaming ability and foam stability. Foaming and foam stability of 0.1% aqueous solutions of each sample at 25°C were measured by the Ross-Miles method (7). Foam stability was calculated based upon changes of foam height from just after dropping (t = 0) to 5 min later (t = 5) (4).

Surface tension lowering. Surface tensions of aqueous solutions at 25°C were measured by an FACE surface tensiometer CBVP-A3 (Kyowa Surface Science, Kyoto, Japan). Critical micelle concentration (CMC) and surface tension at the CMC (γ_{CMC}) were calculated from these data.

Interfacial tension lowering. Interfacial tensions of 0.1% aqueous solutions under *n*-decane, oleic acid, and triolein at 25°C were measured by the same apparatus as used for surface tension.

Wettability. Wetting times for 0.1% aqueous surfactant solutions were measured at 25°C by the Draves method. Wool (100%) felt (3 × 20 cm) (Japan Wool Textile, Osaka, Japan) was used as test cloth.

Solubilization. Solubilization of Yellow OB dye (Tokyo Kasei, Tokyo, Japan) by 0.1% aqueous solutions was evaluated at 25°C by the same method as Nishikido (8).

RESULTS AND DISCUSSION

Cloud point. Figure 3 shows the results of cloud point measurements. Because the terminal end of the EO chain is blocked by a methyl group, EFME shows lower water solubility and has a lower cloud point than AE. The cloud point of C_{12}-NRE, which has a narrow EO adduct distribution, is higher than that of C_{12}-BRE, which has a broad distribution. On the contrary, the cloud point of narrow C_{12}-EFME is somewhat lower than that of broad C_{12}-EFME; so, it seems

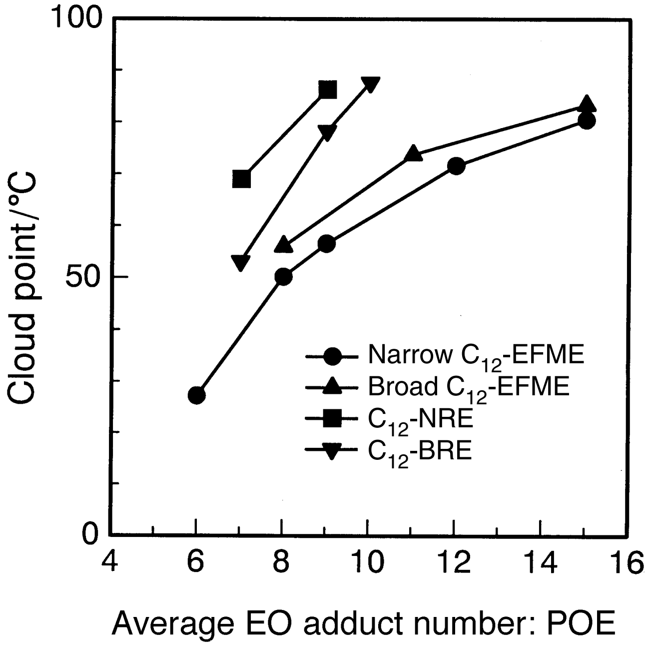

FIG. 3. Cloud point as function of EO adduct number. See Figures 1 and 2 for abbreviations.

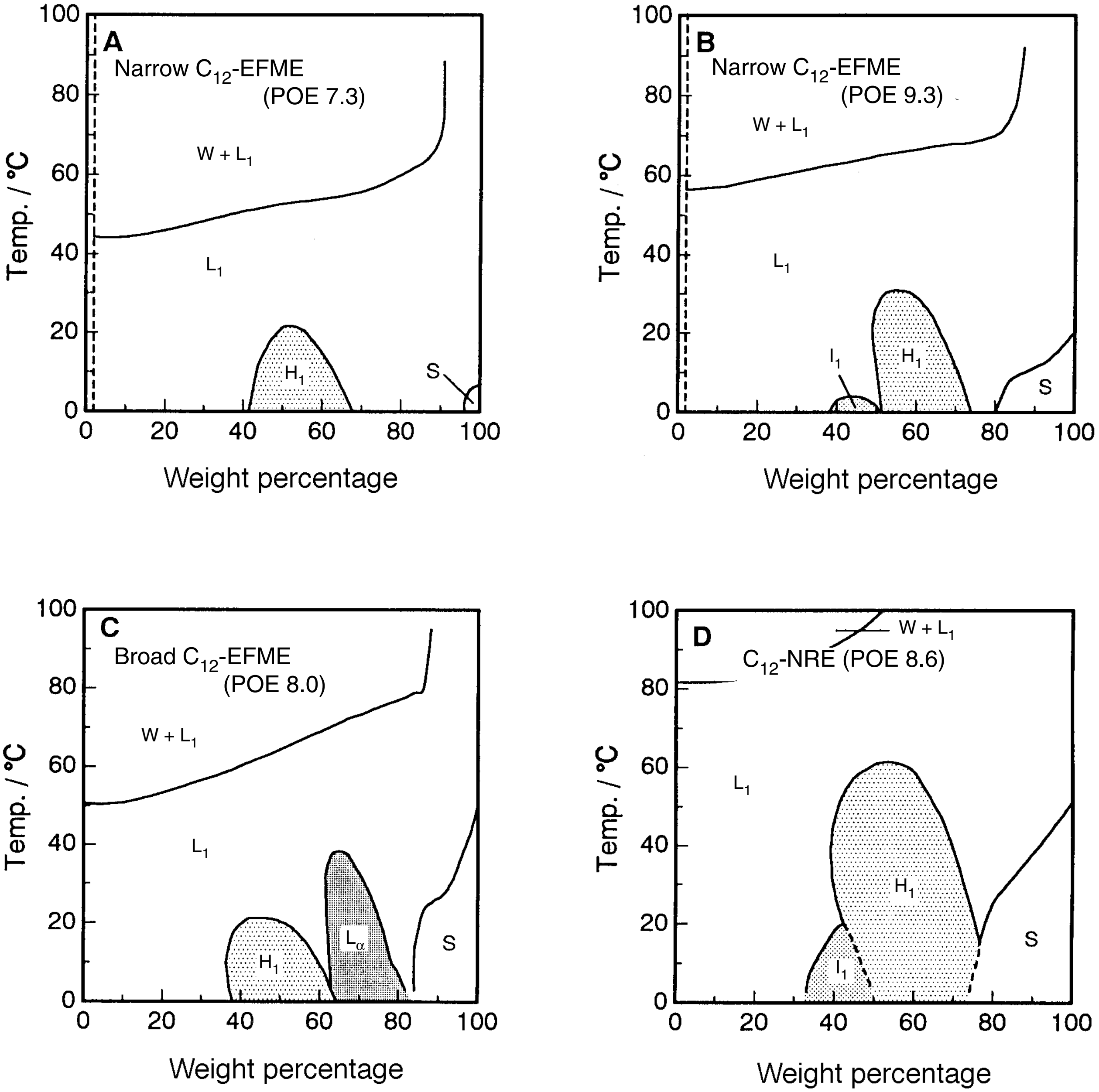

FIG. 4. Phase diagrams of EFME, AE. A: narrow C_{12}-EFME (POE 7.3) Reference 6; B: narrow C_{12}-EFME (POE 9.3) Reference 6; C: broad C_{12}-EFME (POE 8.0); D: C_{12}-NRE (POE 8.6). L_1 = micellar solution; I_1 = small micelle cubic phase; H_1 = hexagonal phase; L_α = lamellar phase; S = hydrated solid; W = dilute surfactant solution. See Figures 1 and 2 for abbreviations.

that the effect of EO adduct distribution on the cloud point of EFME is opposite to that of AE.

Phase diagram. Figure 4 A–D shows phase diagrams for narrow C_{12}-EFME (POE 7.3 and 9.3) (6), broad C_{12}-EFME (POE 8.0), and C_{12}-NRE (POE 8.6). The gelling regions (H, hexagonal phase) for narrow C_{12}-EFME (Fig. 4A and 4B) are noticably smaller than those of C_{12}-NRE (Fig. 4D). Therefore, EFME retains good liquid properties within a wider range of concentration and temperature compared to AE. Also, the gelling regions of narrow C_{12}-EFME (Fig. 4A and 4B) are smaller than those of broad C_{12}-EFME (Fig. 4C). Narrow C_{12}-EFME has no L_α phase and has a smaller solid phase (S) than broad C_{12}-EFME. For a more detailed study of the relationship between molecular structure and gellation, phase diagrams of monodispersed octaoxyethylene dodecylether (C_{12}-SRE) (9), methoxyoctaoxyethylene dodecylether (C_{12}-SRE-Me; the terminal hydroxyl of the EO chain was blocked by a methyl group) (10), and narrow C_{12}-EFME were compared, respectively. As shown in Figure 5, the L_α and V_1 phases (A) disappear when the terminal hydroxyl of the EO chain by a methyl group is blocked by a methyl group (B). The I_1 phase (Fig. 5A and 5B) is not present in Figure 5C, perhaps due to the ester linkage. Therefore, it is conceivable that narrow C_{12}-EFME has a smaller liquid crystal (gelling)

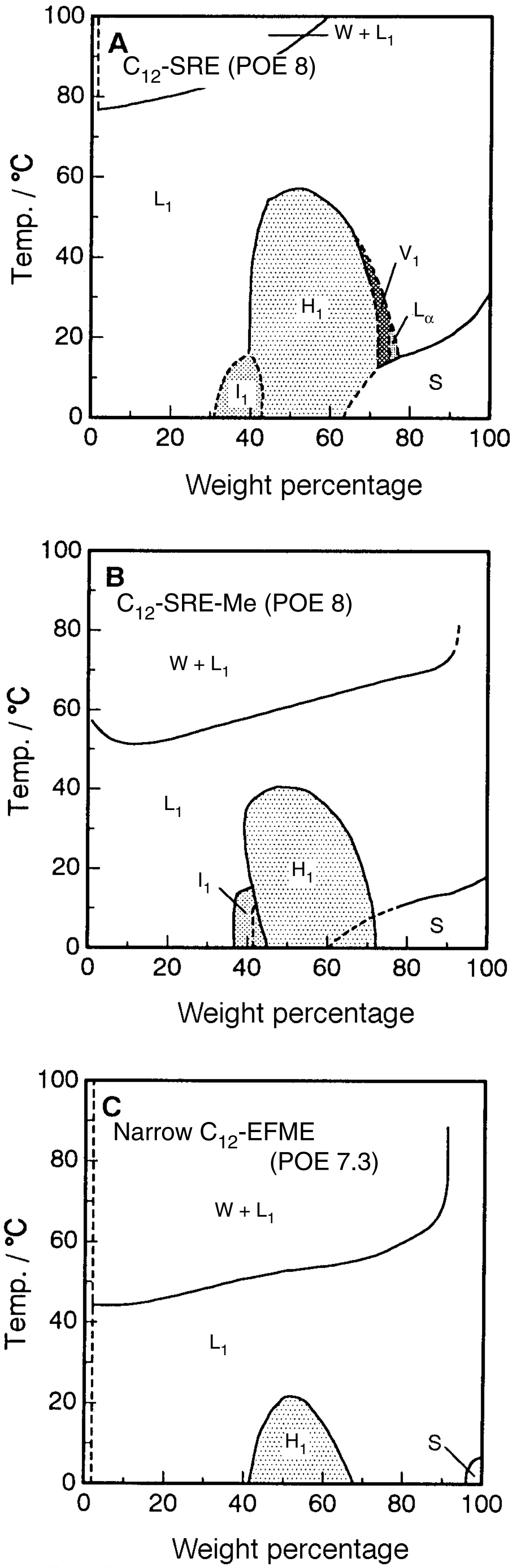

FIG. 5. Effect of molecular structure upon phase diagram. A: C_{12}-SRE (POE 8) Reference 9; B: C_{12}-SRE-Me (POE 8) Reference 10; C: narrow C_{12}-EFME (POE 7.3) Reference 6. V_1 = bicontinuous cubic phase; SRE, single-range ethoxylate. See Figures 1 and 2 for other abbreviations.

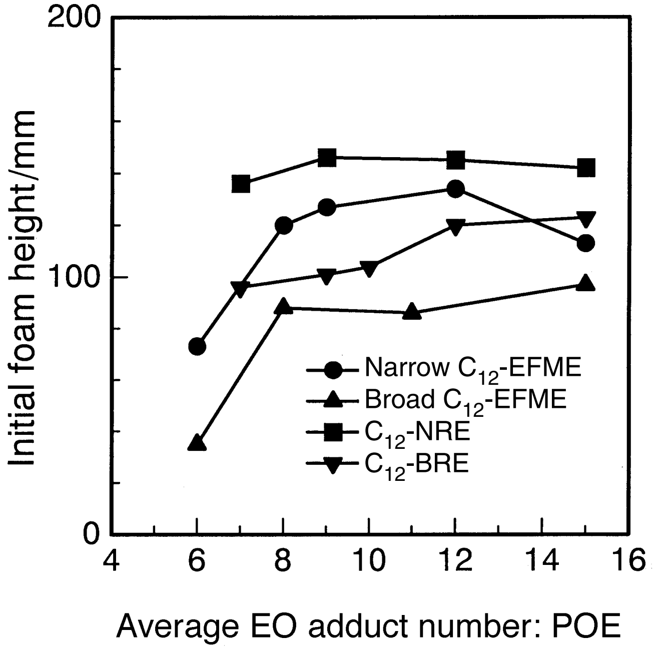

FIG. 6. Initial foam height (foaming ability) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

region because it is difficult for narrow C_{12}-EFME to have compact molecular orientation on account of the double effect of the terminal methyl group and ester bond in the molecule.

Foaming ability and foam stability. Figure 6 shows the initial foam height data from the Ross-Miles method. Foaming ability of narrow C_{12}-EFME is below that of C_{12}-NRE but higher compared to C_{12}-BRE or broad C_{12}-EFME. The presence of the terminal methyl group and ester bond may lower

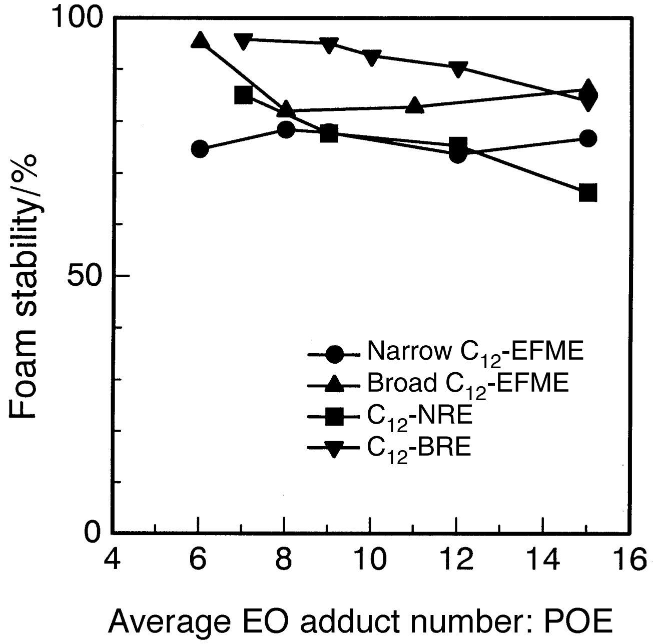

FIG. 7. Foam stability (foam-breaking) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

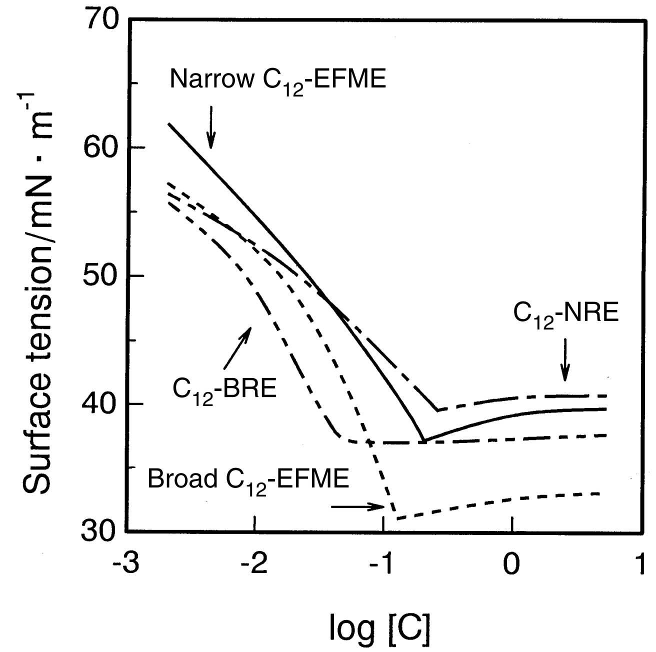

FIG. 8. Surface tension as function of concentration for four different samples. See Figures 1 and 2 for abbreviations.

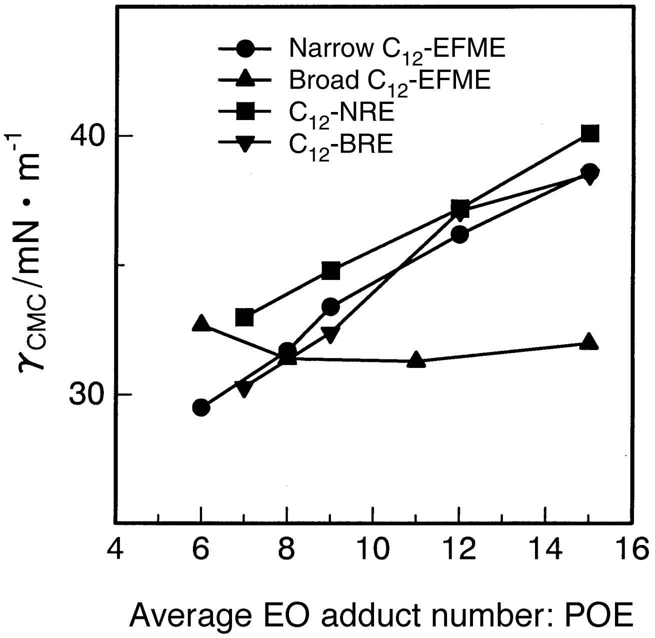

FIG. 10. γ_{CMC} value as function of EO adduct number. See Figures 1 and 2 for abbreviations.

the foaming ability. The foaming ability of narrow C_{12}-EFME is better compared to the broad C_{12}-EFME due to the narrow EO adduct distribution.

Figure 7 shows foam stability. Narrow C_{12}-EFME and C_{12}-NRE have lower foam stability than broad C_{12}-EFME and C_{12}-BRE. For broad C_{12}-EFME or C_{12}-BRE, unreacted raw material and the fractions with fewer EO units tend to hinder foam breaking.

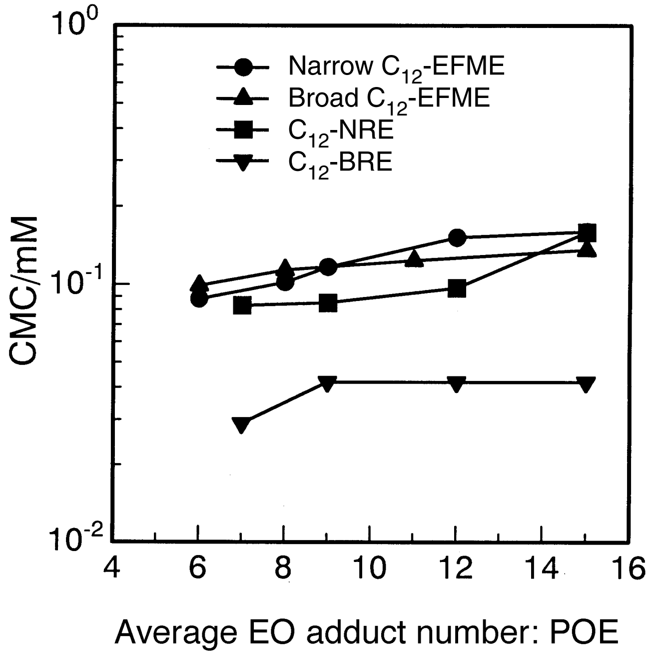

FIG. 9. Critical micelle concentration (CMC) value as function of EO adduct number. See Figures 1 and 2 for abbreviations.

Ability to lower surface tension. Figure 8 shows surface tension curves for those samples whose average EO adduct number is 15. Figures 9 and 10 show CMC and γ_{CMC} values calculated by the Gibbs adsorption equation, respectively. To aid the reader in using these data in the future, the values are summarized in Table 2. The CMC value of C_{12}-BRE is somewhat lower than those of C_{12}-NRE and C_{12}-EFME. The γ_{CMC} values for C_{12}-BRE and narrow C_{12}-EFME are similar and

TABLE 2
CMC and γ_{CMC} Value of Each Sample[a]

	POE	CMC (mM)	γ_{CMC} (mN/m)
Narrow C_{12}-EFME	6	0.088	29.5
	8	0.102	31.7
	9	0.117	33.4
	12	0.152	36.2
	15	0.160	38.6
Broad C_{12}-EFME	6	0.099	32.7
	8	0.114	31.4
	11	0.124	31.3
	15	0.136	32.0
C_{12}-NRE	7	0.083	33.0
	9	0.085	34.8
	12	0.097	37.2
	15	0.159	40.1
C_{12}-BRE	7	0.029	30.3
	9	0.042	32.4
	12	0.042	37.1
	15	0.042	38.5

[a] CMC, critical micelle concentration. See Table 1 for other abbreviations.

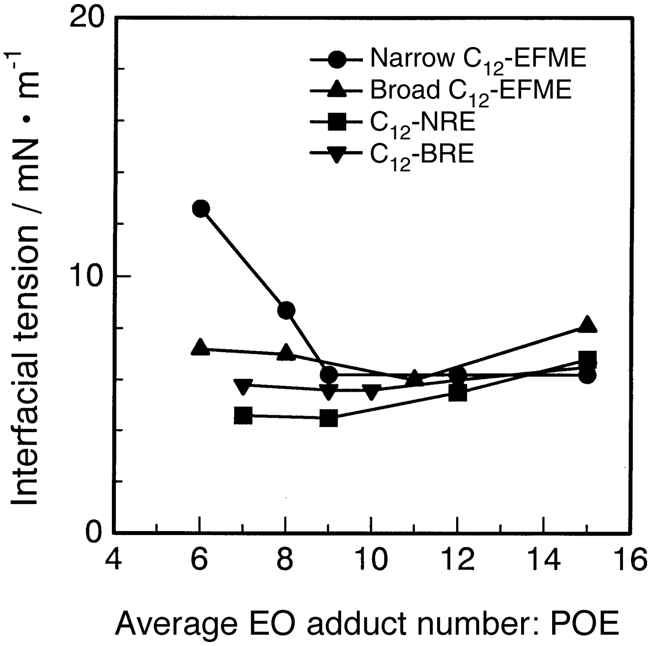

FIG. 11. Interfacial tension (vs. *n*-decane) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

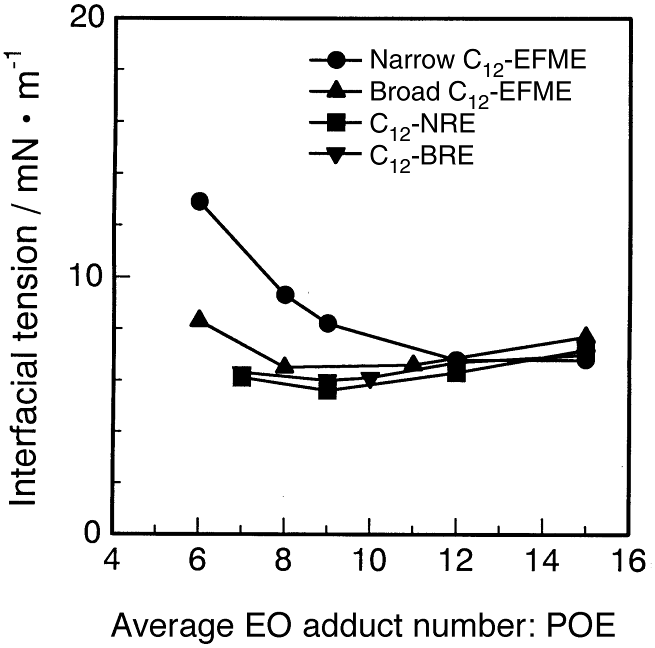

FIG. 13. Interfacial tension (vs. triolein) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

increase with increasing EO content. In contrast, the γ_{CMC} value of broad C_{12}-EFME is generally lower than the others and is little affected by increasing EO content.

Ability to lower interfacial tension. Figures 11 to 13 show interfacial tension values for each sample under oil phases of *n*-decane, oleic acid and triolein, respectively. While each sample shows the similar ability to lower the aqueous interfacial tension with respect to oleic acid, the ability to lower interfacial tension by narrow C_{12}-EFME with *n*-decane and triolein are somewhat lower compared to broad C_{12}-EFME, C_{12}-NRE, and C_{12}-BRE in the range of small average EO adduct number. However, the performance of narrow C_{12}-EFME increases as the average EO level increases.

Wettability. Figure 14 shows the result of wettability measurements. While narrow C_{12}-EFME and C_{12}-NRE show similar wettability, wettability of broad C_{12}-EFME and C_{12}-BRE

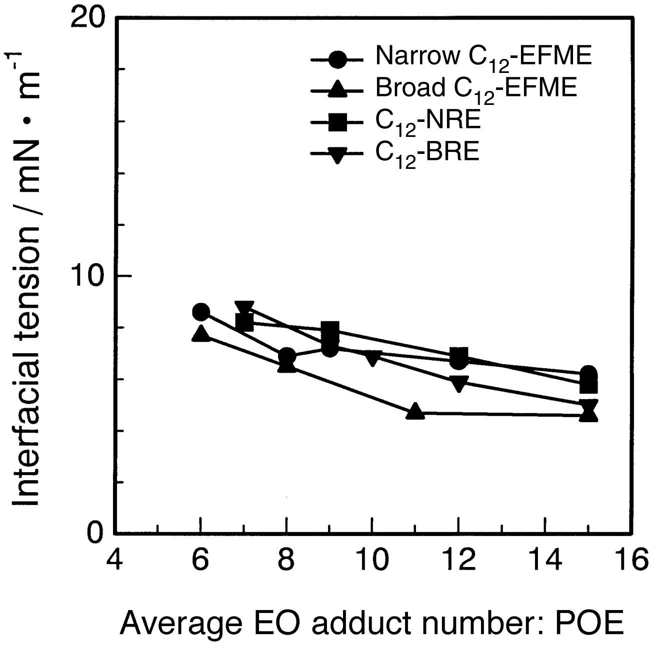

FIG. 12. Interfacial tension (vs. oleic acid) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

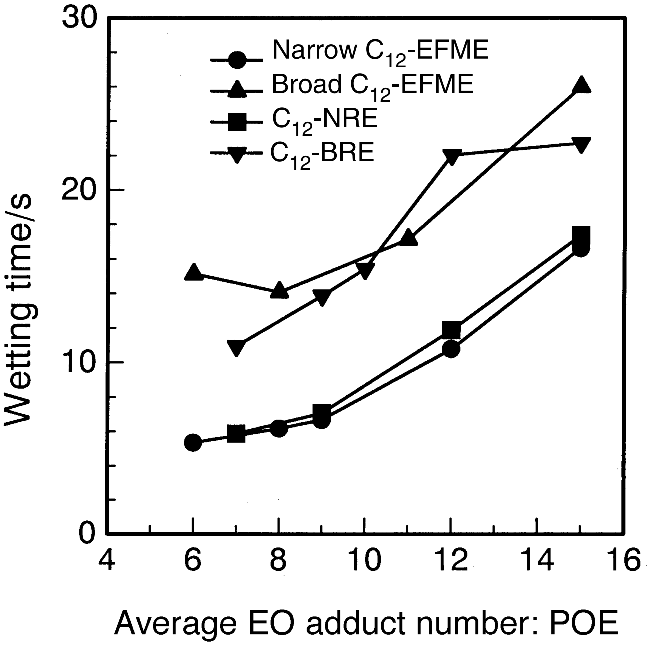

FIG. 14. Wetting time (wettability) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

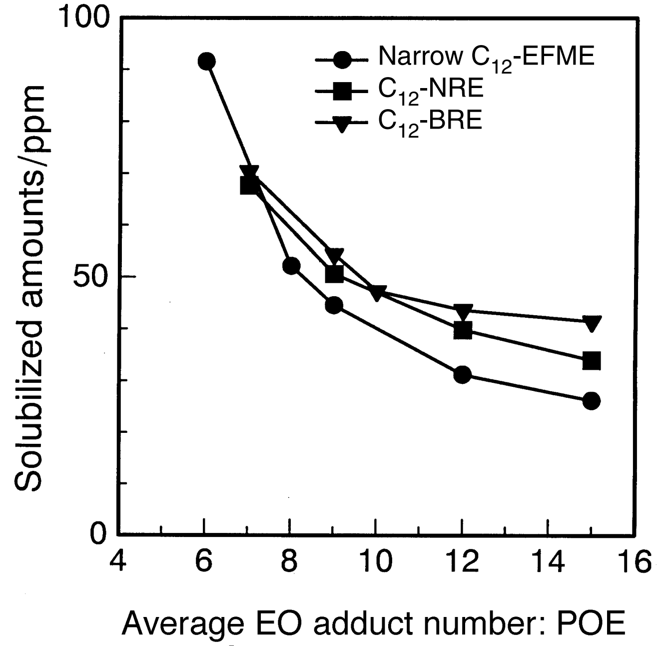

FIG. 15. Solubilization (solubilizate: Yellow OB) as function of EO adduct number. See Figures 1 and 2 for abbreviations.

are somewhat inferior. As wettability tends to decrease with higher average EO adduct number, which results in higher hydrophilicity, fractions of large EO adduct number in broad C_{12}-EFME and C_{12}-BRE are considered to hinder wetting.

Solubilization. Figure 15 shows the solubilization in each sample by using Yellow OB as solubilizate. In the range of higher average EO adduct number, solubilization of dye with C_{12}-EFME is a little lower than that of C_{12}-NRE and C_{12}-BRE. Reasoning for this may be that the terminal methyl group of C_{12}-EFME hinders the transfer of Yellow OB into the micelles. In the range of lower average EO adduct number, however, both EFME and AE show similar solubilization.

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