The Determination of the Poly(oxyethylene) Oligomer Distribution in a Nonionic Surfactant by Means of Thin-Layer Chromatography

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Synopsis. The analytical method for determining the distribution of the polymerization degree of the oxyethylene (OE) chain in commercially available poly(oxyethylene) alkyl ether (C_mE_n) was investigated by means of thin-layer chromatography with flame-ionization detection (TLC-FID). It was found that the method of calculating the relative response factors of every OE chain to FID could be determined, and the analysis of the distribution of the polymerization degree of the OE chain in commercially available C_mE_n became possible using the TLC-FID method.

It is known that the distribution as well as the mean length of the oxyethylene (OE) chain in nonionic surfactants greatly affects various surface-chemical characteristics.[1-3] Gas chromatography and high-performance liquid chromatography are now used as general analytical methods for determining the distribution of the polymerization degree of the OE chain.[4-6] Considering the time required for the analysis and the use of a detector, it is difficult to operate every routinely the instruments in order to acquire reproducible data. The present authors have recently reported an advanced separating method of the OE chain using thin-layer chromatography with flame-ionization detection (TLC-FID) as a rapid alternative method.[7] It is necessary to find the relative response factor of each peak to the hydrogen ionization detector (FID) and to correct it in order to determine the real distribution of the polymerization degree of the OE chain from the chromatogram drawn.

The method of calculating the relative response factor of a alkyl ether-type nonionic surfactant to FID and the method of analyzing the distribution of the polymerization degree were investigated in this study. This method should also be applicable for the determination of polyethylene glycol as a by-product in poly(oxyethylene)-type nonionic surfactants.

Experimental

Materials. The poly(oxyethylene) alkyl ether (C_mE_n: $C_mH_{2m+1}O(C_2H_4O)_nH$) with a single chain length and a relatively narrow distribution of OE[8] was obtained from the Nikko Chemicals Co., Ltd. Guaranteed reagents of benzene, ethyl acetate, and acetic acid were used as the developing solvents.

Measurement by TLC-FID. The TLC-FID instrument, the thin-layer rod, and the analytical conditions were the same as those described in a previous report.[7]

Results and Discussion

Calculation of Relative Response Factor. Figure 1 illustrates the relationship between the OE-chain length (n) in C_mE_n with a single-chain length and the peak area (A) in the TLC-FID chromatogram. When the alkyl-chain lengths (m) are the same, the relationship between A per gram and n is linear. The relationship between A and n in each C_mE_n can, therefore, be expressed by the following formula:

$$A = -Pn + b \quad (1)$$

where P is the slope for each straight line in Fig. 1, b is the A of the corresponding higher alcohol, and b is proportional to m, as is shown in Fig. 1. The relationship between P and m in C_mE_n is also linear, as is shown in Fig. 2. This relationship is represented by the following equation:

$$P = 0.095m - 0.50 \quad (2)$$

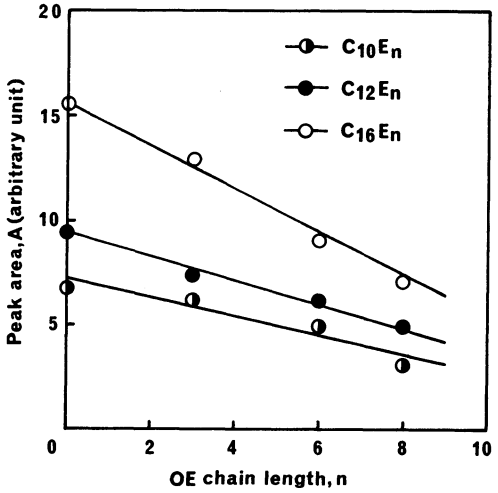

Fig. 1. Relationship between OE chain length in nonionic surfactant and peak area.

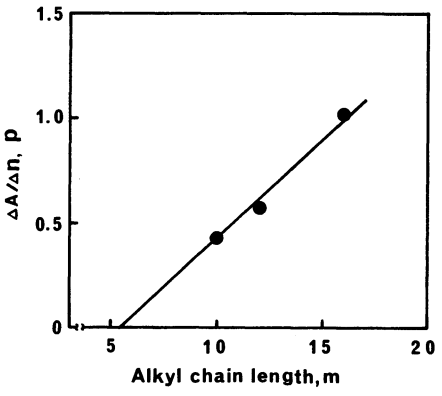

Fig. 2. Plots of P vs. m according to Eq. 2.

Table 1. OE Distribution and Statistical Analysis of Commercially Available $C_{12}E_5$ (n=4)

OE number	Relative response factors	Molar distribution	Weight distribution	SD/X(%)
1	1.00	0.0109	0.0062	13.1
2	1.08	0.0523	0.0354	4.2
3	1.17	0.1552	0.1220	2.2
4	1.28	0.2224	0.1990	1.1
5	1.41	0.2113	0.2120	1.6
6	1.58	0.1525	0.1696	0.7
7	1.78	0.0974	0.1189	2.0
8	2.05	0.0526	0.0699	5.2
9	2.41	0.0305	0.0438	6.3
10	2.92	0.0149	0.0231	9.9

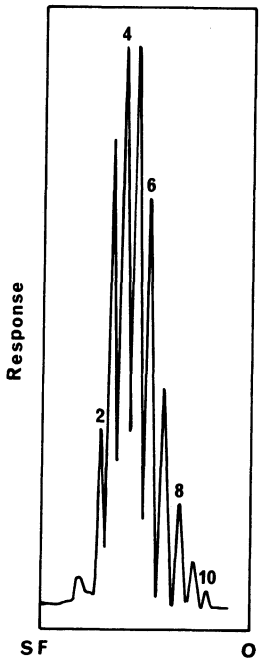

Fig. 3. TLC-FID chromatogram of commercially available $C_{12}E_5$. The peak number corresponds to the number of OE chains. SF: solvent front, O: origin. Mobile phase: 1st development, benzene–ethyl acetate (6/4, vol%), 10 cm; 2nd development, ethyl acetate–acetic acid–water (8/1/1, vol%), 8 cm; gas flow: H_2, 160 mL min^{-1}; air, 2 L min^{-1}; scanning speed: 35 s/scan.

The A value per gram of C_mE_n and the relative response factors of C_mE_n to FID can be calculated from Eqs. 1 and 2. This analytical method is applicable to C_mE_n with m and n values that satisfy $A>0$.

As compared with the previous TLC-FID method,[7] one can calculate the relative response factors of the OE chain for a series of C_mE_n by this method. This method is also widely applicable to the determination of the OE-chain distribution of nonionic surfactants.

Analysis of Chromatogram. Figure 3 shows the TLC-FID chromatogram of commercially available $C_{12}E_5$. Each peak in the chromatogram was identified by using each C_mE_n with a single-chain length. The results indicate that the peaks were detected in the order of the added number of moles of the OE chains. The peaks are satisfactorily separated in the chromatogram. The actual molecular weight distribution was determined using the chromatogram and the relative response factors calculated from Eqs. 1 and 2. The relative response factors are defined as the ratio of the A value per gram of each $C_{12}E_n$ to that of $C_{12}E_1$. All the values were measured relative to $C_{12}E_1$ ($C_{12}E_1$=1.00). The results are shown in Table 1. The table shows that the molecular weight distribution of commercially available $C_{12}E_5$ can be accurately determined. Since the TLC-FID method is a simple, rapid method of analysis requiring no chemical modification, as was stated in the previous report,[7] it is useful for determining the distribution of the OE chain in a poly(oxyethylene)-type nonionic surfactant. In addition, the distribution of the OE chain in any series of C_mE_n can be determined because the relative response factor can be calculated, even for commercially unavailable products,[9] with a single chain. Therefore, the TLC-FID method can be applied to the determination of the OE-chain distribution in other poly(oxyethylene)-type nonionic surfactants by selecting appropriate developing solvents.

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