SURFACTANTS & DETERGENTS

Effects of Molecular Weight Distribution of Nonionic Surfactants on Stability of O/W Emulsions

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From the relationship between the distribution width of oxyethylene (OE) or alkyl chains and O/W emulsions stability, it became evident that even with the same average OE or alkyl chain lengths, the phase-inversion temperature (PIT) and O/W emulsion stability depend on width. However, emulsification at the PIT invariably results in a very stable O/W emulsion. Emulsifiers with a large distribution width of OE or alkyl chains were also found to improve O/W emulsion stability.

In our previous paper, a new method for determining the oxyethylene (OE) chain distribution of nonionic surfactants was reported (1). The OE chain distribution of nonionic surfactants has significant influence on surface chemical properties, such as emulsification and solubility (2,3). It has been found in some studies that O/W emulsions made with emulsifiers of broader distribution are more stable than those made with emulsifiers with sharp distribution (3,4). However, the relationship between O/W emulsion stability and OE chain distribution is not adequately understood, because the average number of OE chains differs and the number of comparative samples is few.

In this paper, the effects of OE and alkyl chain distribution on O/W emulsion stability were examined using emulsifiers with the same numbers of OE and alkyl chains.

EXPERIMENTAL

Materials. The nonionic surfactant samples, homogeneous poly (OE) alkyl ethers (C_mE_n, where m is the number of alkyl chains, n is the number of OE chains) were obtained from Nikko Chemicals Co., Ltd. (Japan). Purity, according to gas chromatography (GC), exceeded 95%. The cyclohexane used was of extra pure grade and used without further purification.

Emulsifiers. The distribution of OE and alkyl chains of the emulsifiers for emulsification is summarized in Table 1, and is indicated as molar distribution. The average numbers of alkyl and OE chains of emulsifiers were 12 and 6, respectively.

Methods. The emulsions consisted of 48 wt% water, 48 wt % cyclohexane and 4 wt% emulsifier. The emulsification was conducted according to Shinoda *et al.* (4). Emulsion storage temperature was 15°C or 25°C. The phase volumes of the coalesced, drained and emulsion phases were observed after 24 hr. The phase-inversion temperature (PIT) of each emulsion was determined by an electric conductivity device (5).

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TABLE 1

Distribution of Nonionic Surfactants Used for *Emulsification*

	Distribution of oxyethylene chain length				
Emulsifiers	$C_{12}E_4$	$C_{12}E_5$	$C_{12}E_6$	$C_{12}E_7$	$C_{12}E_8$
$C_{12}E_6$	—	—	1.0	—	—
$C_{12}E_6$(S)	—	0.1	0.8	0.1	—
$C_{12}E_6$(N)	0.05	0.10	0.70	0.10	0.05
$C_{12}E_6$(W)	0.1	0.2	0.4	0.2	0.1
$C_{12}E_6$(R)	0.13	0.19	0.26	0.39	0.03
$C_{12}E_6$(L)	0.03	0.39	0.26	0.19	0.13

	Distribution of alkyl chain length		
Emulsifiers	$C_{10}E_6$	$C_{12}E_6$	$C_{14}E_6$
$C_{12}E_6$	—	1.0	—
$C_{12}(S)E_6$	0.1	0.8	0.1
$C_{12}(W)E_6$	0.3	0.4	0.3

*Distribution is molar distribution.

RESULTS AND DISCUSSION

Figure 1 shows the effects of the distribution width of OE chain length on O/W emulsions stability stored at 25°C. The broadly distributed emulsifiers showed higher PIT than the sharply distributed emulsifiers. Emulsification at PIT invariably formed very stable O/W emulsions, as already pointed out by Shinoda and Saito (6). One reason for this may be the smaller interfacial tension between the oil and water phases around the PIT (7). Emulsification at a temperature higher than PIT formed O/W emulsions more stable than those produced below PIT. Emulsification at a temperature higher than PIT gave a W/O emulsion at first, which then underwent an inversion to an O/W emulsion by cooling to the storage temperature. During this time, emulsifiers dissolved in the oil phase moved to the water-oil interface from the oil phase and may have found important use at the water-oil interface. Thus, emulsification at a temperature higher than PIT may enhance O/W emulsion stability. As for a correlation between the distribution width of OE chains and O/W emulsion stability, the O/W emulsion made with a homogeneous emulsifier ($C_{12}E_6$) was the most unstable, and that made with an emulsifier having a large width of OE distribution [$C_{12}E_6$(W)] was quite stable. The reason for this may be that broader emulsifiers are more surface active, as previously reported (8). The effects of the distribution shift of OE chains on O/W emulsion stability stored at 25°C are shown in Figure 2. The O/W emulsion made with $C_{12}E_6$(R), having distribution in the longer OE chain direction, was much more stable than that with $C_{12}E_6$(L),

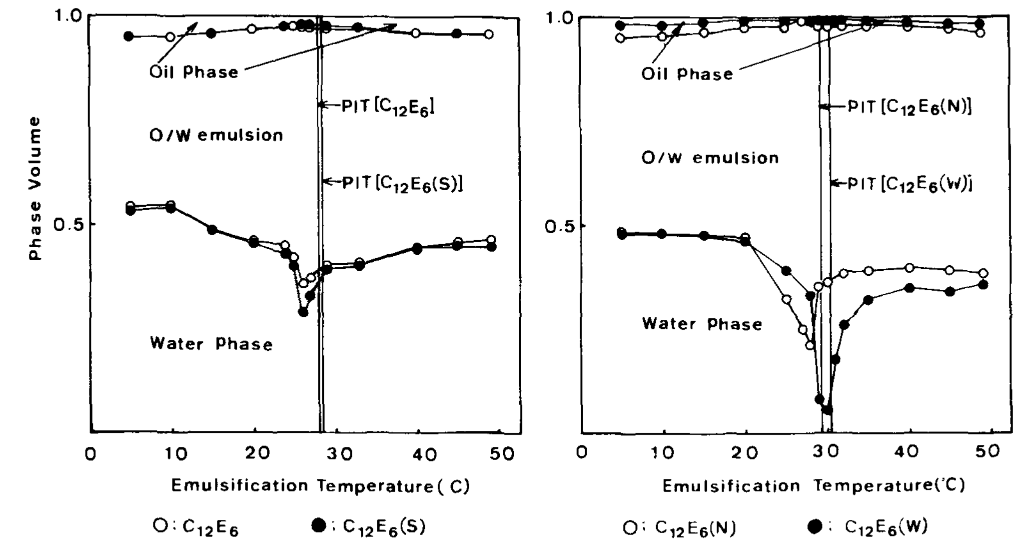

FIG. 1. Effect of distribution width of OE chains on O/W emulsions stability stored at 25°C.

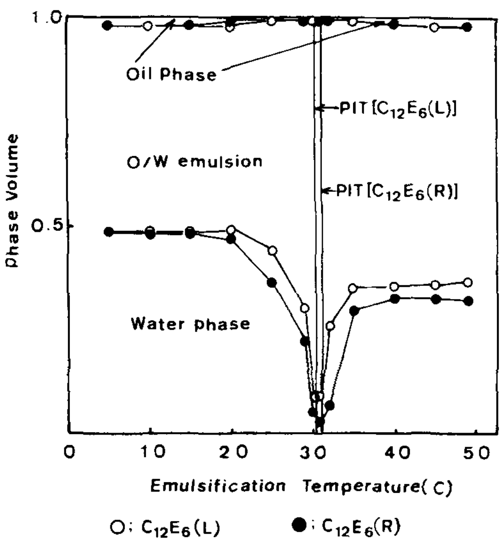

FIG. 2. Effect of distribution shift of OE chains on O/W emulsions stability stored at 25°C.

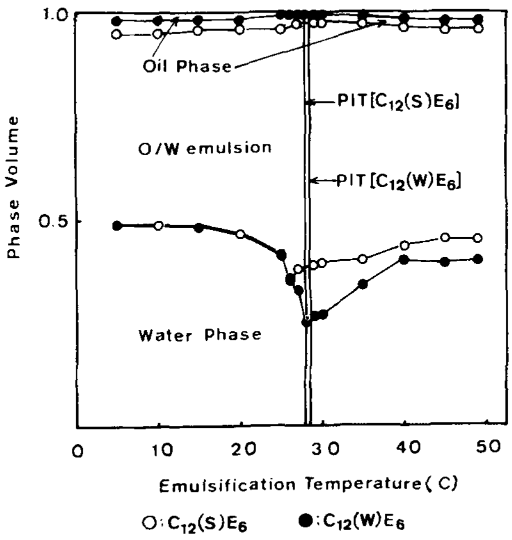

FIG. 3. Effect of distribution width of alkyl chains on O/W emulsions stability stored at 25°C.

having distribution in the shorter OE chain direction. Thus, $C_{12}E_7$ and $C_{12}E_8$, having longer OE chains, contribute to the formation of stable O/W emulsions. Figure 3 shows the effects of the distribution of alkyl chains on O/W emulsion stability stored at 25°C. When the distribution of alkyl chains was broad, the coalescence was slight and the emulsions were much more stable than that by sharply distributed emulsifiers. Figure 4 shows the effects of OE and alkyl chain lengths on PIT, as well as the stable temperature region of O/W emulsions stored at 25°C by homogeneous C_mE_n. The stable temperature region is defined as follows: The coalesced phase is not recognized, and the remaining O/W emulsion phase is above 70% after 24 hr. PIT increased linearly with OE chain length, but decreased with increase in alkyl chain length. For O/W emulsions made with $C_{12}E_6$, there was coalescence at all emulsification temperatures (5-60°C), while for those made with $C_{12}E_7$, $C_{12}E_8$ and $C_{10}E_6$, a stable temperature region could be detected. The stable temperature region of $C_{12}E_4$, $C_{12}E_5$ and $C_{14}E_6$ could not be determined, since the storage temperature of the O/W emulsions exceeded PIT. It thus follows that the formation of more stable emulsions by broadly distributed emulsifiers may be due to further expansion of the stable temperature region caused by mixing various chain lengths.

The effects of the distribution width of OE and alkyl chains on O/W emulsion stability at 15°C are presented in Figure 5. Compared to O/W emulsions stored at 25°C, the distribution of OE and alkyl chains failed to have strong effects on O/W emulsion stability at 15°C. However, the broadly distributed emulsifiers gave more stable O/W emulsions than the sharply distributed emulsifiers. Figure 6 shows PIT and the stable temperature region of O/W emulsions stored at 15°C by homogeneous C_mE_n. The

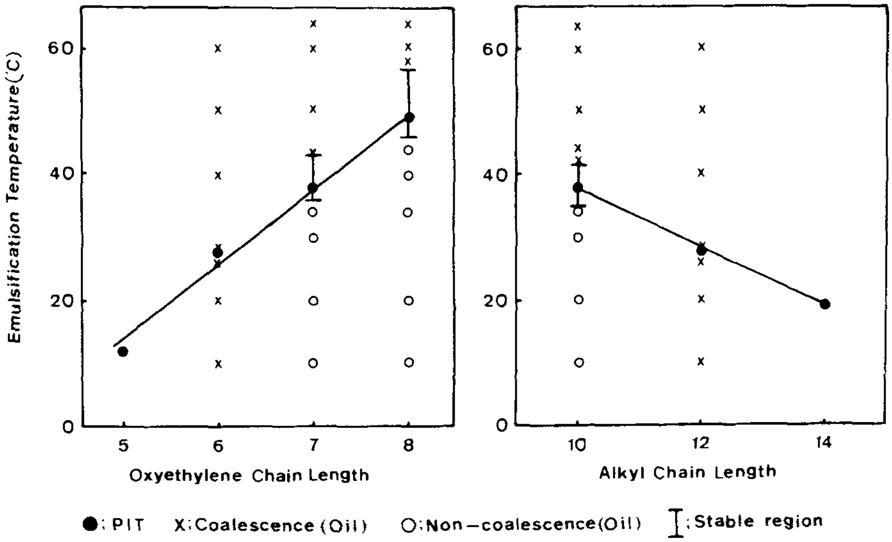

FIG. 4. PIT and stable temperature region of O/W emulsions stored at 25°C by homogeneous C_mE_n.

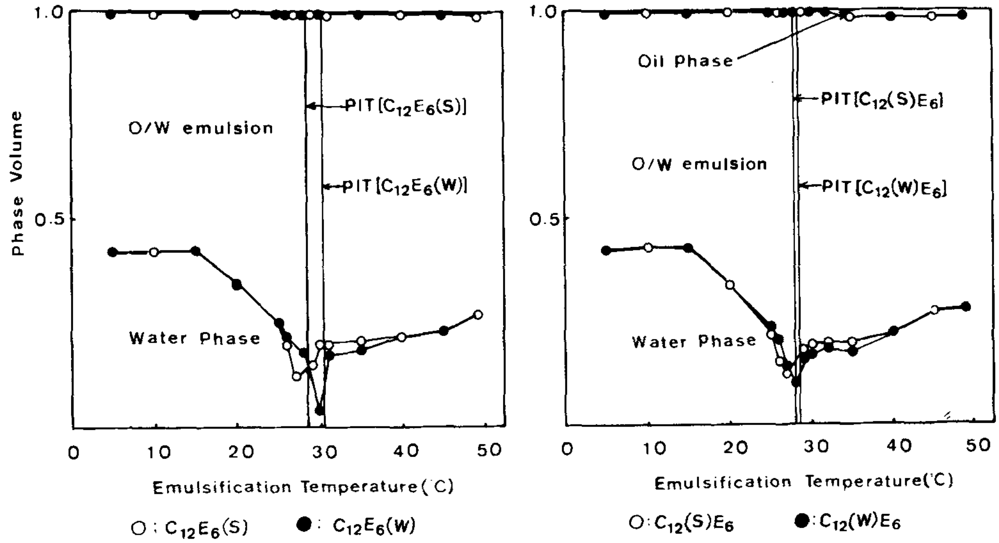

FIG. 5. Effect of distribution width of OE and alkyl chains on O/W emulsions stability stored at 15°C.

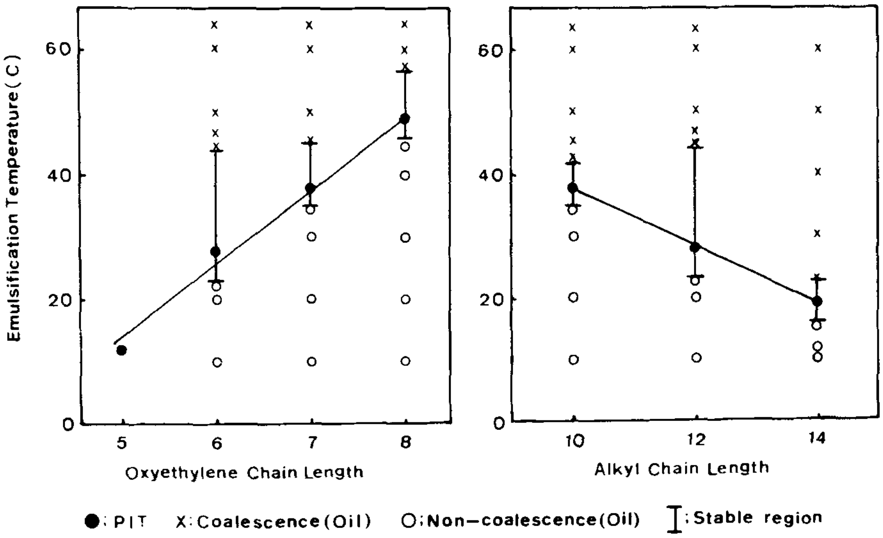

FIG. 6. PIT and stable temperature region of O/W emulsions stored at 15°C by homogeneous C_mE_n.

stable temperature region of O/W emulsions by homogeneous C_mE_n stored at 15°C was generally constant as compared with that for storage at 25°C, especially with $C_{12}E_6$. $C_{12}E_6$ is an optimal emulsifier for a cyclohexane-water system since the HLB value of $C_{12}E_6$ and that required for cyclohexane are 11.7 and 11.5, respectively (9). Therefore, it appears that $C_{12}E_6$ contributes principally to the elevation of O/W emulsion stability at 15°C. $C_{12}E_6$, however, does not contribute to the formation of stable O/W emulsions at 25°C. This is because PIT of $C_{12}E_6$, as shown in Figure 4, is near the storage temperature (25°C) and coalescence proceeds very rapidly near PIT as reported by Shinoda *et al.* (6).

From the results of this study, we have concluded that the mixing of emulsifiers having short or long OE and alkyl chains is effective for enhancing O/W emulsion stability, since the stable temperature region expands.

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