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Influence of Dialkyl Ethers on the Surface Properties of Homogeneous Nonionic Surfactants

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ABSTRACT

Influence of the trace amounts of the corresponding dialkylethers on the surface and colloidal properties of the pure polyoxyethylene alkyl ethers were studied. The dialkyl ether, undetected by gas liquid chromatography (GLC) was found by gel permeation chromatogram (GPC) as the corresponding impurity in homogeneous pure polyoxyethylene alkyl ether and confirmed using infrared (IR), nuclear magnetic resonance (NMR) and mass spectroscopy (MS). After removing the corresponding impurity in each surfactant with a GPC separation column, the minima in the surface tension curves disappeared completely. Adding the corresponding dialkyl ether to the pure surfactant produced the minima in the surface tension curves and large values for surface aging, cloud points were lowered more than for the pure surfactants and foam height and foam stability for the aqueous solutions decreased gradually.

INTRODUCTION

Several workers have so far reported studies on the basic surface and colloidal properties of homogeneous nonionic surfactants (1), and have pointed out that these properties are affected by the distribution of the ethylene oxide chain length in the molecules and by small amounts of unreacted alcohol contained as an impurity (2). In order to obtain more distinct information about the surface and colloidal properties of nonionic surfactants in general, we need to employ nonionic surfactants with homogeneous ethylene oxide chain length having no distribution.

Recently, we synthesized some nonionic surfactants with homogeneous ethylene oxide chain length by Williamson's method (3) and confirmed the existence of trace amounts of the corresponding diether as by-product, as reported by Mulley et al. (4).

However, the complete separation of the diether from the corresponding surfactants has not been reported so far and the influence of the diether remaining as an impurity on the surface and colloidal properties of the corresponding surfactant has not been studied so far.

In this paper, we will report the confirmation of a diether, the purification of the surfactants and their influence on surface and colloidal properties.

EXPERIMENTAL

Materials

A series of octaoxyethylene glycol n-alkyl ethers C_nH_{2n+1}-$O(CH_2CH_2O)_8H$, (C_nE_8; n = 10, 12 and 14) was prepared from the corresponding n-alkyl alcohols and tetraethylene glycol by Williamson's method (3) and were purified by recrystallization. The homogeneity of the surfactants was confirmed by gas liquid chromatography (GLC) to be in excess of 99.0%. Traces of impurity undetected by GLC were removed by repeated passage through a gel permeation chromatographic column, Hitachi Model 635 (stainless-steel tubes packed with porous polymer gel of Shodex H 202), at a flow rate of 3.0 mL/min, using $CHCl_3$ as solvent until the minimum in the surface tension curves and the corresponding peak in the Gel Permeation Chromatogram (GPC) disappeared.

The identical process was used to purify all samples. Separated impure materials were found to be the corresponding dialkyl ethers contained as by-products by means of nuclear magnetic resonance (NMR), mass spectroscopy (MS) and IR. These dialkyl ethers were white, crystalline and slightly soluble in water. Water was purified by passing it through a Milli-Q system (Nihon Millipore Co.) until its specific conductivity fell below 10^{-1} . Ω^{-1} . cm^{-1}.

MEASUREMENTS

Surface tensions of surfactant solutions prepared by dilution of the mother liquor were measured at 25 C with a Wilhelmy-type surface tensiometer, Shimadzu Model ST-1.

The stability of a foam produced by shaking a 50 mL graduated cylinder containing 10 mL surfactant solutions at several concentrations was evaluated by the following changes of foam height against time.

Cloud points were measured on C_nE_8 micellar solutions containing different amounts of the corresponding dialkyl ethers in the closed system in a glass tube. The solutions were heated or cooled at the rate of 1 C every 1-2 min under agitation.

Each cloud point was determined by noting the onset of cloudiness on heating.

RESULTS AND DISCUSSION

Figure 1 shows the gel permeation chromatogram for $C_{10}E_8$ obtained by repeated crystallization. The existence of a small peak in Figure 1 suggests the existence of a trace of by-product of the corresponding compound as an impurity in the nonionic surfactant.

As with $C_{10}E_8$, the chromatograms for $C_{12}E_8$ and $C_{14}E_8$ gave the same result. Furthermore, the existence of impurities for these surfactants has been confirmed by the appearance of a minimum in the surface tension curves as shown in Figure 2a-b but not in Figure 2c, where the curve has no minimum.

After removing the corresponding impurities in each surfactant, using the GPC separation column, the minima in the surface tension curves disappeared completely as shown in Figure 2a-b.

CMC values were: 1.0×10^{-1}M for $C_{10}E_8$, 7.1×10^{-5}M for $C_{12}E_8$ and 9.0×10^{-6}M for $C_{14}E_8$.

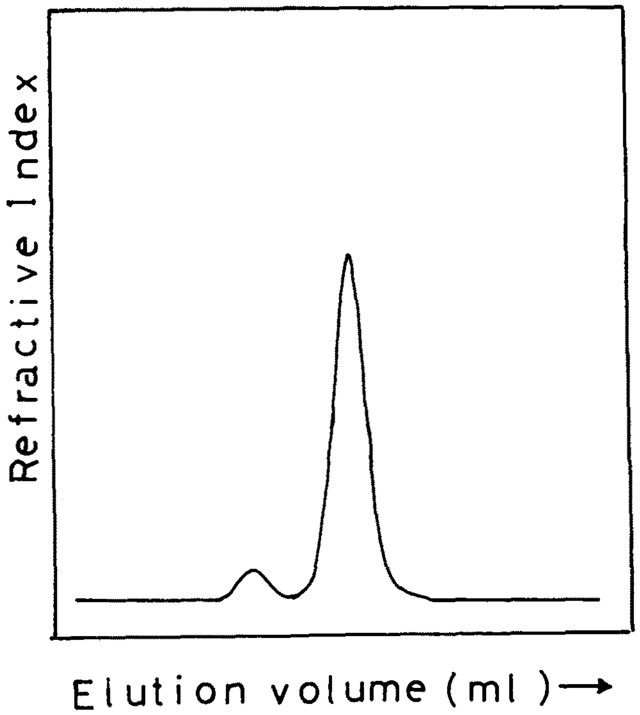

FIG. 1. Gel permeation chromatogram of original $C_{10}E_8$.

In general, as reported by Williamson (3), the corresponding dialkyl ethers may be formed as impurities by a reaction as follows:

$$2\ RO(C_2H_4O)_4Cl + NaO(C_2H_4O)_4Na \xrightarrow{\qquad} RO(C_2H_4O)_{12}R + 2NaCl \quad [1]$$

As the IR spectra for each dialkyl ether did not show the absorbance of hydroxyl group, this reaction can reliably be disregarded.

Figure 3a-c shows the variation with time of the surface tensions in the aqueous solutions with or without dialkyl ethers below and above the CMC. The surface tension values for the aqueous solutions containing impurities decrease markedly with time below the CMC, but those for pure $C_{10}E_8$ and $C_{12}E_8$, except $C_{14}E_8$, hold constant, as

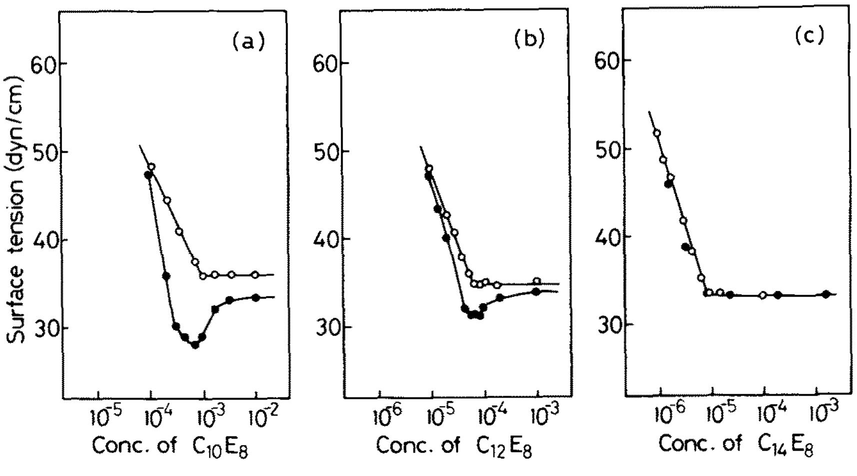

FIG. 2. Surface tension-concentration curves for (a) $C_{10}E_8$, for (b) $C_{12}E_8$ and for (c) $C_{14}E_8$. (○) contains the impurity, and (●) is pure nonionic surfactant.

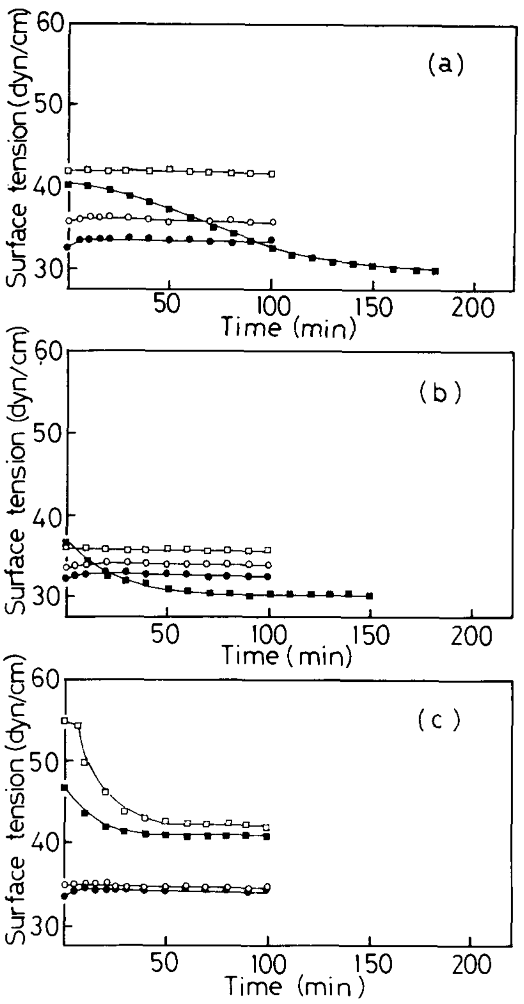

FIG. 3. Time dependence on surface tensions for pure nonionic surfactants and for those containing the impurity. (□) and (○) are for pure nonionics below and above CMC, (■) and (●) are for the impurity-containing nonionics.

shown in Figure 3a-b. This fact suggests that the impurity is more surface active than the corresponding pure nonionic surfactant, and gives strong support to the suggestion that the corresponding dialkyl ethers are formed as the impurity in the reaction of equation [1].

Figure 4 shows the cloud points for mixed aqueous solutions consisting of pure C_nE_8 and the corresponding dialkyl ethers with total concentration of 0.1%, as a function of the concentration of the corresponding dialkyl ethers. As these values decrease linearly with increasing concentration of the corresponding dialkyl ether, this implies that the dialkyl ethers are more hydrophobic than those of the corresponding pure C_nE_8.

This hydrophobicity was also observed in the effect of the addition of dialkyl ether on the foam stability of the pure $C_{10}E_8$ as shown in Figure 5. Figure 5 shows the foam height and stability, as defined by equation [2].

$$\text{foam stability} = \frac{\text{(foam height after 5 min. [cm])}}{\text{(foam height initial 0 min [cm])}} \times 100 \quad [2]$$

for mixed solutions consisting of pure $C_{10}E_8$ and corresponding dialkyl ethers with total concentrations of 0.01 and 0.1% as functions of the corresponding dialkyl ether. Both foam height and stability decreased with the increase in the concentration of $C_{10}E_{12}C_{10}$ as the impurity. Consequently, as traces of the dialkyl ether are contained in the corresponding pure C_nE_8 as the impurity, we have found that the dialkyl ether markedly affects the surface active properties of C_nE_8.

These effects are presumably caused by the strong surface-active properties and the structure with more hydrophobic parts, which have 2 long hydrocarbon chains at both ends of ethylene oxide chain.

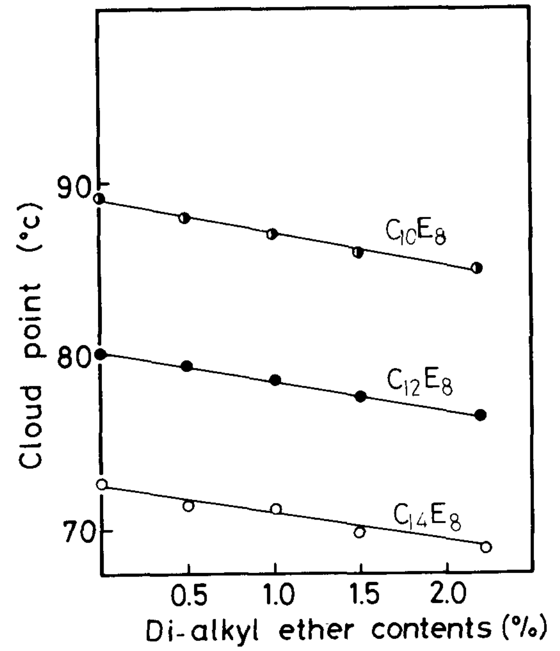

FIG. 4. Effect of dialkyl ether as an additive on cloud point.

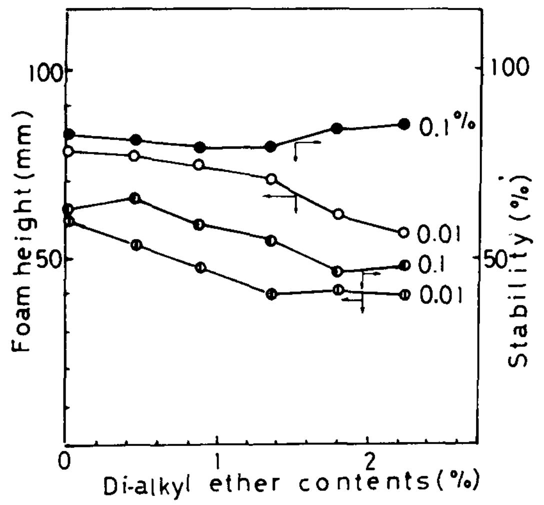

FIG. 5. Effect of added dialkyl ether on foam properties. (●) and (◐) are 0.1% and 0.01% for foam stability and (○) and (◐) are 0.1 and 0.1% for foam height.

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