point temperatures have been proven both to be indicative of the intensity of the spray tower exhaust opacity and to be suitable for a quality control criterion for assessing the acceptability of individual nonionic raw material receipts.

The smoke point test can be viewed as a visual vapor pressure test. The thin, continuous stream of smoke is a direct result of a constant quantity of material vaporizing and recondensing. The temperature at which this occurs is directly related to the vapor pressure of a particular nonionic. The relationship between the smoke point temperature and vapor pressure is defined by the Clausius-Clapeyron equation.

The effect of paraffin impurities in the starting alcohol has not been addressed. Although present at very low levels in the final alcohol ethoxylate, they do contribute to the observed plume. The paraffin composition will reflect the alcohol composition. The contribution to pluming will be reduced by increased ethoxylation level as a result of simple dilution. The effect of free alcohol is the major item affecting organic loading in current operations and the one which can be most readily controlled. Therefore, the effect of paraffin impurities has been set aside for this discussion.

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♣Changes in Physico-Chemical Properties During Decomposition of Nonionic Surfactant Solutions

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The decomposition and accompanying changes in surface chemical properties of nonionic surfactants were investigated. The decomposition of nonionic surfactants occurs in the polyoxyethylene and ester chains. Ester chains were susceptible to decomposition with an increase in the polyoxyethylene chain length, but polyoxyethylene chains were not. Surface chemical properties such as solubilizing power, surface tension, effective specific volume, and intrinsic viscosity also deteriorated during decomposition of the surfactants.

Knowledge of surfactant decomposition is of fundamental importance in understanding the stability of solubilizates. We have reported previously that the oxidation stability of benzaldehyde derivatives in aqueous solutions of nonionic surfactants is affected by micellar structure (1,2). Hamburger et al. (3) also found that surfactant decomposition has a pronounced effect on the stability of solubilizates. Surfactant decomposition, including biodegradation as well as chemical decomposition, has been studied extensively (4-6). However, nonionic surfactant decomposition still is not clearly understood (7,8).

In this paper, we report on the decomposition and accompanying changes in surface chemical properties of nonionic surfactants in solution.

EXPERIMENTAL

Materials. Polyoxyethylene monostearates (PMS-n, n = 25, 45, 55, where n is the average number of ethyleneoxide groups) were obtained from Nikko Chemicals Co. Ltd. These nonionic surfactants were purified by extraction (1). Other reagents were extra pure grade and were used without further purification. Only double-distilled ion-exchanged water was used.

Methods. Surfactant solutions (15 ml, 5×10^{-3} M) were kept in 30 ml corked glass tubes at 40 ± 0.1 C. The surfactant concentrations were well above their cmc (2).

The cloud point was determined by heating a solution containing NaCl (1 M) in a test tube and recording the temperature at which the solution became turbid. The NaCl lowered the cloud point to below the boiling point (3).

Peroxides were determined by the iodometric spectrophotometric method of Azaz et al. (9).

Conductivity and pH were measured using a conductivity meter (Takemura Electric Works Ltd., Model DM-37) or a pH-meter (Central Kagaku Co., Model HG-3), respectively. Turbidity was measured using a turbidimeter with an integrating sphere (Nihon Seimitsu Kogaku Co. Ltd., Model SEP-H). The degree of the turbidity was calculated using the following formula:

$$\text{Turbidity } (\%) = \text{Td}/\text{Tt} \times 100$$

where Td is diffused transmittance and Tt is total transmittance.

Stability of ester chains was determined by the method of Samejima et al. (10).

The solubilizing power of PMS-n was determined in terms of solubility of Orange OT by the method of Al-Saden et al. (11). Surface tension measurement was made using a Wilhelmy plate and torsion balance (Kyowa

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Kagaku Co. Ltd., Model CBVP-P). Viscosity was measured by a Cannon-Fenske viscometer.

RESULTS AND DISCUSSION

Decomposition of hydrophilic chain. PMS-n decomposition ensues on the polyoxyethylene chains, but effects of chain length on the decomposition of the polyoxyethylene chains were not recognized (Figs. 1-3).

The cloud point is expected to be the criterion for sensitivity in changes of the polyoxyethylene chains of PMS-n, because the cloud point of nonionic surfactants is related to the number of the polyoxyethylene units (3). Changes in cloud point of PMS-n aqueous solutions are shown in Figure 1. The cloud point of each PMS-n declined with time and decreased about 3.5 C after 21 days. Sample solutions ⩾21 days old could not be measured because they became turbid. The gradual shortening of the polyoxyethylene chains of PMS-n is inferred from the above results. Hydroperoxides of each PMS-n were formed in short periods and the so-called termination period was reached within about 15 days, then decreased (Fig. 2).

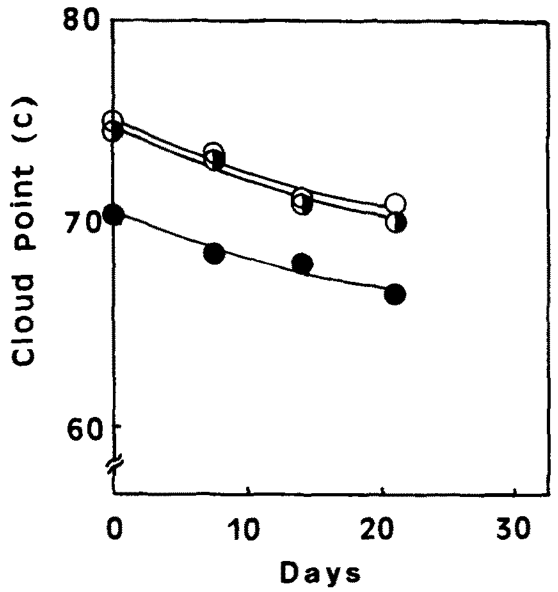

FIG. 1. Changes in cloud point of PMS-n aqueous solutions stored at 40 C (●:PMS-25; ◑:PMS-45; ○:PMS-55).

Hamburger et al. (3) reported similar results for cetomacrogol decomposition. Hydroperoxides are formed on the α-carbon atoms of the polyoxyethylene chains and the decomposition of hydroperoxides gives short-chain products such as aldehydes and acids (3). The pH fell and the conductivity rose with time in PMS-n aqueous solutions (Fig. 3). After 28 days, the pH values of each PMS-n fell into the range of 2.9–3.1, and the conductivity values were between 0.15–0.16 micromho/cm. Acid formation normally indicates an end reaction of oxidation.

Decomposition of hydrophilic and hydrophobic binding chains. The results on the decomposition of hydrophilic and hydrophobic binding chains (ester chains) are shown in Figures 4 and 5. The ester chains were susceptible to decomposition with an increase in the polyoxyethylene chain length of PMS-n.

After about seven days, the turbidity increased with an increase in the polyoxyethylene chain length of PMS-n (Fig. 4). The turbidity of PMS-45 and PMS-55 was approximately 2 and 3 times as high as that of the PMS-25 after 28 days, respectively. The turbidity probably resulted from the stearic acid liberated by hydrolysis. The method of hydroxamic acid (10) is capable of determining the remainder of ester chains or the degree of hydrolysis because it is based on the reactivity of ester chains and hydroxylamine. Each PMS-n was degraded by a pseudo-first order reaction (Fig. 5). The rate constants (K) increased with an increase in the polyoxyethylene chain length of PMS-n. K of PMS-45 and PMS-55 were about 2 and 10 times as large as that of PMS-25, respectively.

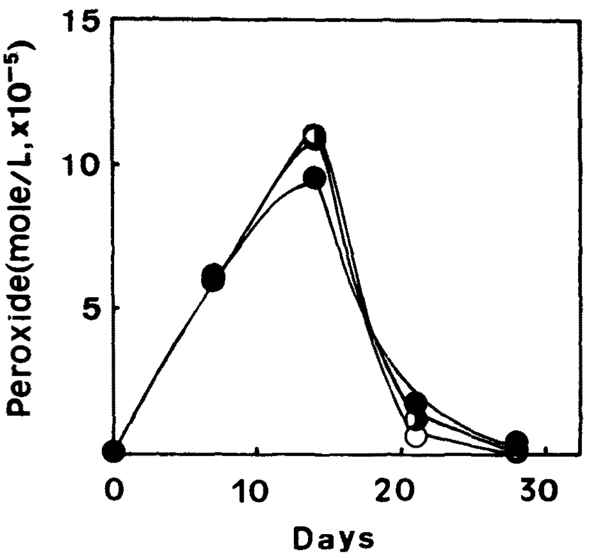

FIG. 2. Changes in peroxide formation of PMS-n aqueous solutions stored at 40 C (●:PMS-25; ◑:PMS-45; ○:PMS-55).

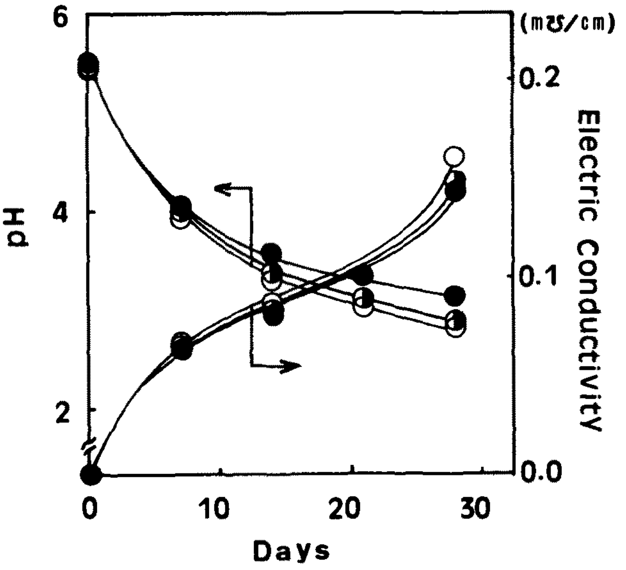

FIG. 3. Changes in pH and electric conductivity of PMS-n aqueous solutions stored at 40 C (●:PMS-25; ◑:PMS-45; ○:PMS-55).

Loss of surfactant properties. Decomposition of PMS-n would be expected to influence a number of physicochemical properties, so changes in solubilizing power, surface tension and viscosity of PMS-n were investigated. The solubilizing power of PMS-n decreased with time, and each PMS-n was reduced to about 70% from the initial values (Fig. 6). This indicates a shortening of the polyoxyethylene chains because the solubilizing efficiency of the nonionic surfactants for Orange OT increases with an increase in the concentration and polyoxyethylene chain length (12).

The surface tension of PMS-n decreased gradually with time (Fig. 7). The surface tension tends to decrease with an increase in the polyoxyethylene chain length of PMS-n. Decrease of the surface tension would be due to absorption at the air-water interface of insoluble products formed by decomposition (13).

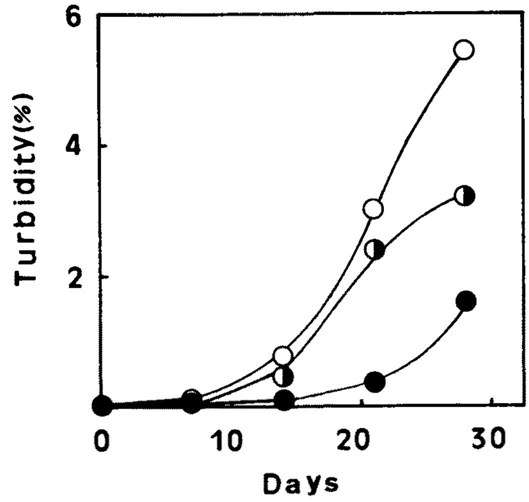

FIG. 4. Changes in turbidity of PMS-n aqueous solutions stored at 40 C (●:PMS-25; ◑:PMS-45; ○:PMS-55).

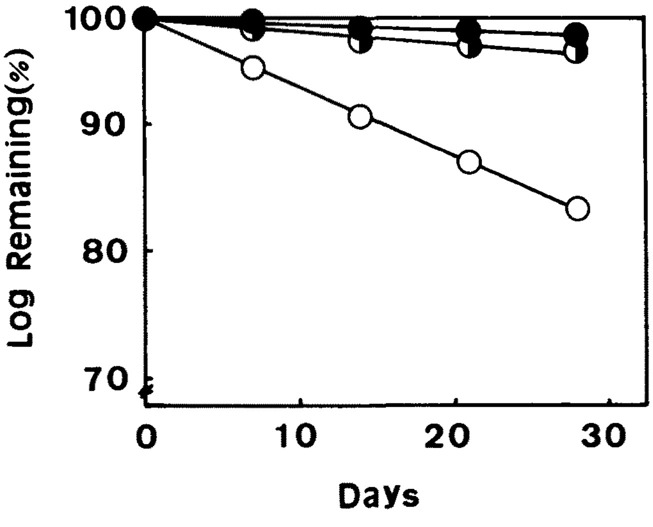

FIG. 5. Stability of PMS-n stored at 40 C [●:PMS-25, K = 0.7 × 10^{-3} (day^{-1}); ◑:PMS-45, K = 1.2 × 10^{-3} (day^{-1}); ○:PMS-55, K = 6.7 × 10^{-3} (day^{-1})].

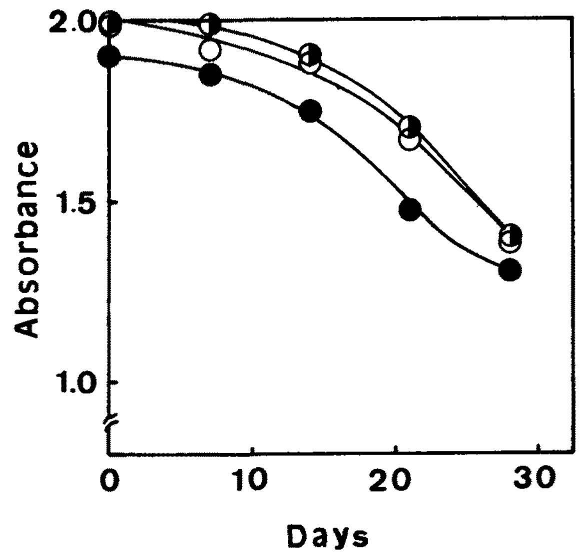

FIG. 6. Changes in solubilization of Orange OT in PMS-n aqueous solutions stored at 40 C (●:PMS-25; ◑:PMS-45; ○:PMS-55).

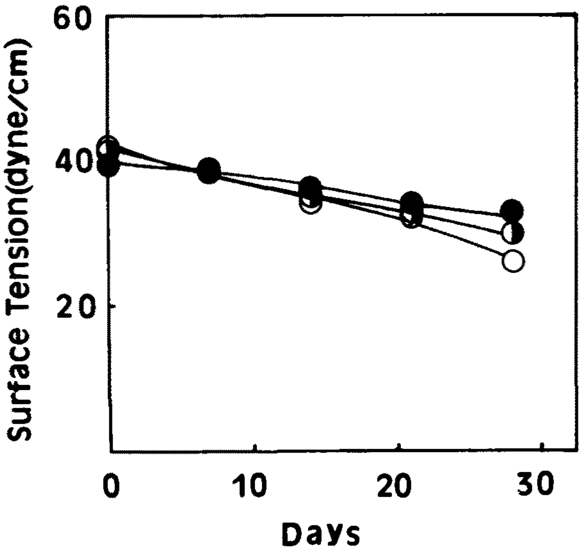

FIG. 7. Changes in surface tension of PMS-n aqueous solutions stored at 40 C (●:PMS-25; ◑:PMS-45; ○:PMS-55).

TABLE 1

Effective Specific Volumes and Intrinsic Viscosities of PMS-n Aqueous Solutions Stored at 40 C

Surfactants	1st day	15th day	30th day
PMS-25	V:2.7, $[\eta]$:0.036	V:2.5, $[\eta]$:0.030	V:2.3, $[\eta]$:0.029
PMS-45	V:3.3, $[\eta]$:0.080	V:2.9, $[\eta]$:0.056	V:2.5, $[\eta]$:0.051
PMS-55	V:3.8, $[\eta]$:0.088	V:3.5, $[\eta]$:0.078	V:3.1, $[\eta]$:0.075

The effective specific volume (V) and the intrinsic viscosity $[\eta]$ of PMS-n are shown in Table 1, where V was evaluated in accordance with the previous paper (2). V and $[\eta]$ decreased with time. From the results, it was concluded that the shape of PMS-n micelles remains spherical (14) in spite of the decomposition and the shortening of the polyoxyethylene chains take place.

We found that the decomposition of PMS-n takes place in the polyoxyethylene and ester chains, and concurrently there are changes in the surface chemical properties of the PMS-n. In addition, ester chains of PMS-n decompose faster with an increase in polyoxyethylene chain length. In a recent paper (15), we reported that the aggregation number decreases with an increase in the polyoxyethylene chain length of PMS-n, while the micellar volume, the hydration and the micellar inner polarity increase. This means that the increase in the polyoxyethylene chain length leads to more hydrophilic and looser micelles. This also implies that interactions between ester chains and OH^- or H_3O^+ ions are greater at a longer polyoxyethylene chain length.

The decomposition of the nonionic surfactants is thought to be responsible for solubilizates instability in micellar systems. That is to say, hydroperoxides and carboxylic acid formations would induce decomposition of solubilizates liable to oxidation and acid-catalyzed reactions. Knowledge of the experimental results of this paper may be of a fundamental guide on stability of solubilizates in micellar systems.

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