

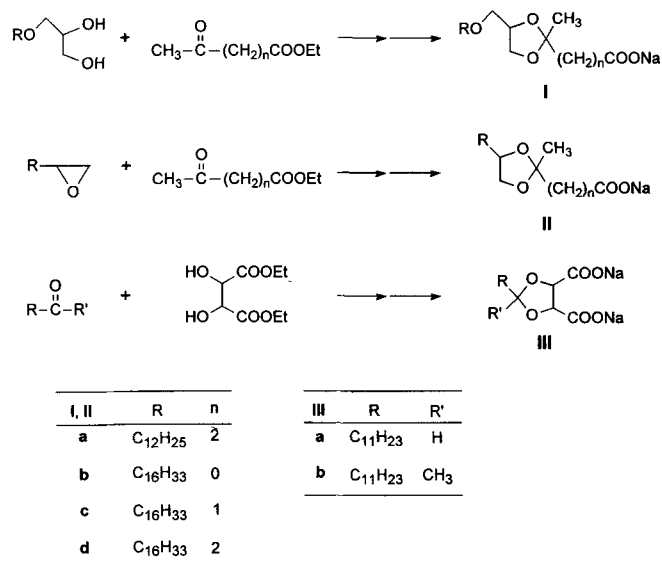
Biodegradation of Different Carboxylate Types of Cleavable Surfactants Bearing a 1,3-Dioxolane Ring

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ABSTRACT: The biodegradability of new carboxylate types of "acid-sensitive" cleavable surfactants bearing a 1,3-dioxolane ring was measured by the biochemical oxygen demand (BOD) method in the presence of activated sludge. The result for sodium dodecanoate, measured under the same conditions, was used as a standard for evaluating the biodegradability of these cleavable surfactants. For cleavable surfactants derived from epoxides and oxocarboxylates, the biodegradation was considerably influenced by the length of the lipophilic alkyl chain, the presence of the oxymethyl moiety in the lipophilic group, and the number of methylene units between the dioxolane ring and the carboxylate group. For another type of cleavable surfactant, 2-(long-chain alkyl)-1,3-dioxolane-4,5-dicarboxylate, the biodegradation rate for the compound, bearing a proton at position 2 in the dioxolane ring, is faster than that for the corresponding compound bearing a methyl group at position 2. *JAOCs* 72, 853–856 (1995).

KEY WORDS: Acid decomposition, biodegradability, biodegradation, carboxylate-type surfactants, cleavable surfactants.



SCHEME 1

We have studied the preparation and properties of various types of "acid-sensitive" chemocleavable surfactants (1–9). They are designed to decompose into nonsurface-active species under acidic conditions after fulfilling their original functions. Recently, we have developed three carboxylate types of cleavable surfactants (**I**, **II**, and **III** in Scheme 1) bearing a 1,3-dioxolane ring. The first type of compound (**I**) was obtained by the reaction of 1-*O*-alkylglycerols with oxocarboxylates (7), and the second type (**II**) was prepared from alkyl epoxides and oxocarboxylates (9). The presence or absence of an ether oxygen atom in the side chain is the structural difference between surfactants **I** and **II**. The last type of surfactant (**III**), which has two carboxylate groups, was synthesized from diethyl tartrate and fatty carbonyl compounds (8). These compounds can be prepared from readily accessible starting materials without any expensive reagents or special equipment. We have clarified that the 1,3-dioxolane ring makes a positive contribution to surface-active properties

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(7–9). In this work, we measured the biodegradability of some of these chemocleavable surfactants because surfactants are now desired that have good biodegradation from an ecological standpoint (10–18). We will discuss the effect of structure of these chemocleavable surfactants on their biodegradability.

EXPERIMENTAL PROCEDURES

Materials. Three types of target surfactants (**I**, **II**, and **III**) were synthesized according to the reported methods (7–9). They were isolated by recrystallization from ethanol or reversed-phase column chromatography with methanol as an eluent. Sodium dodecanoate, aniline, and *n*-dodecylbenzenesulfonate were commercial products (Wako Pure Chemical Ind., Ltd., Osaka, Japan). The sodium dodecanoate (chemical reagent grade) was isolated by recrystallization from ethanol. The others (extra pure reagent grade) were used without further purification.

Methods. The biodegradability of the surfactants was evaluated by the oxygen consumption method. The procedure was carried out according to the guidelines of the Japanese law for biodegradation of novel chemical compounds. The test sample was added to a dispersion of activated sludge in the basic culture solution (300 mL). The basic culture solution was prepared according to the Japan Industrial Standard (JIS) K0102. The concentrations of the sample and the activated sludge were 100 (wt/vol) and 30 ppm (wt/vol), respectively. The activated sludge was obtained from a municipal sewage treatment plant in Osaka City. The suspended solids concentration was about 10,000 ppm after 30-min standing. A culture dispersion, containing only activated sludge (30 ppm), was prepared as a blank (300 mL). A dispersion, containing aniline instead of the test sample and activated sludge in the basic culture solution, was prepared as a standard (300 mL). The concentration of aniline was the same as that of the test sample. These culture systems were placed in 500-mL culture bottles and were stirred vigorously at 25°C for 14 d. The change in the biochemical oxygen demand (BOD) (mg) of the systems was monitored with time. The biodegradability was estimated by:

$$\text{biodegradability (\%)} = (\text{BOD} - \text{blank}) / \text{TOD} \times 100 \quad [1]$$

where "blank" refers to the oxygen consumption (mg) and TOD refers to the theoretical oxygen demand (calculated value, mg). If the biodegradability of aniline after one week was not more than 40%, the experiment would be invalidated. The quantity of oxygen consumption was measured with a Coulometer OM-2000 (Ohkura Electronic Co., Tokyo, Japan), which is a BOD meter for closed systems. Oxygen was supplied to the systems by electrolysis of CuSO_4 solution, and the BOD was evaluated from the quantity of electricity used. So the change in BOD of the systems could be monitored with time.

RESULTS AND DISCUSSION

The biodegradability of aniline after one week was above 40% in each experiment; therefore, it was judged that the activated sludge used in this work was effective for the biodegradation of organic compounds. Each experiment was repeated at least three times, and the results are reported as averages of the three values. The deviations from the means were less than 5% of the value given.

The biodegradability of surfactants **Ib**, **Ic**, and **Id**, which are derived from 1-*O*-hexadecylglycerol, is shown in Figure 1, with the result of sodium dodecanoate measured under the same conditions. The biodegradation curve for surfactants **Ib–d** from the initial stages up to about five days is in marked contrast to the result from sodium dodecanoate. For the latter compound, the increase in the degradation curve (up to two days) is relatively steep. On and after the third day, the degradation gradually increases at a constant rate. On the contrary, the biodegradation rate of surfactants **Ib–d** is slow up to two

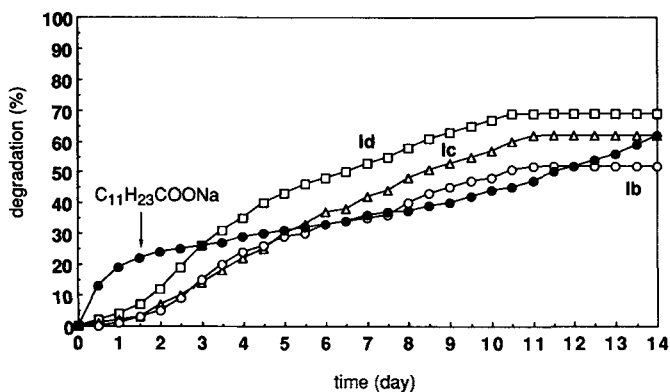


FIG. 1. Biodegradability time course curve for **Ib**, **Ic**, **Id**, and sodium dodecanoate.

days, but on and after the third day, the slope of the degradation curve is about twice as great as that of the sodium dodecanoate curve. The biodegradability of surfactants **Ib–d** becomes essentially constant on and after the eleventh day. The order of the biodegradability after fourteen days is **Id** > **Ic** = sodium dodecanoate > **Ib**.

The results for surfactants **Ia** and **IIa**, bearing a dodecyl group, and for **Id** and **IIc**, bearing a hexadecyl group, all of which were derived from revulinate, are shown in Figure 2. The only difference in structure between surfactants **I** and **II** is the presence or absence of an oxymethylene group in the side chain. Surfactants **Ia** and **IIa** have higher biodegradability by 15% than the corresponding **Id** and **IIc**. However, for **II**, the biodegradability of **IIc** bearing a hexadecyl group is 15% higher than that of **IIa**, for up to about seven days. The reason for this is not clear. The degradability of the **I** surfactants is 15% larger than that of **II**, bearing the corresponding lipophilic alkyl group. This means that the oxymethylene group in the side chain has a positive effect on biodegradation. After fourteen days, the biodegradability of **Id**, bearing a hexadecyl group, is almost the same as that of **IIa**, which contains a shorter dodecyl chain. It was shown previously that the oxymethylene group in the side chain contributes to the hydrophilicity of this type of molecule (9). These results suggest that the higher the hydrophilicity becomes, the better the

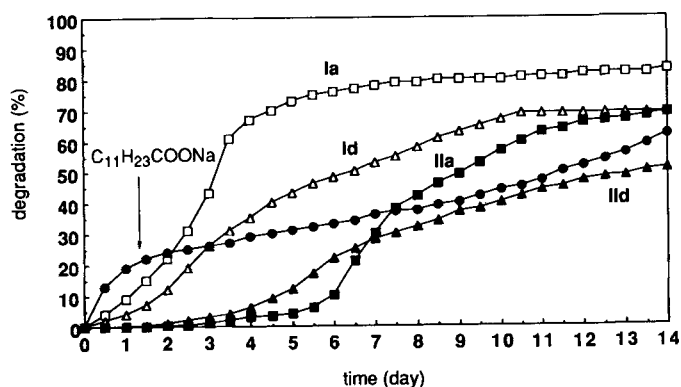


FIG. 2. Biodegradability time course curve for **Ia**, **Id**, **IIa**, **IIc**, and sodium dodecanoate.

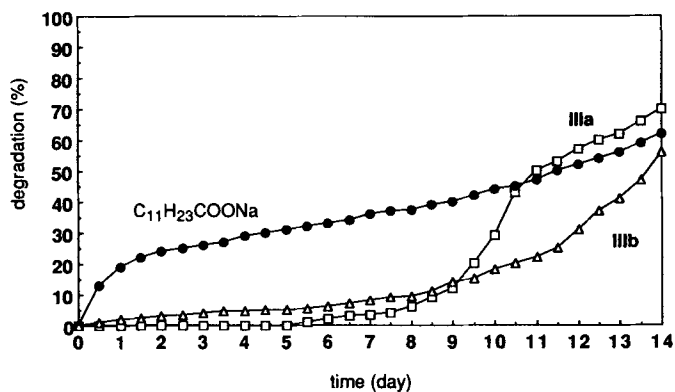


FIG. 3. Biodegradability time course curve for **IIIa**, **IIIb**, and sodium dodecanoate.

degradability of these types of compounds. Another noticeable point is that a lag time is observed in the biodegradation of compounds **IIa** and **IIb**. These compounds, however, are gradually decomposed even on and after the eleventh day, unlike **Ia** and **Id**.

Figure 3 illustrates the biodegradability of the *bis*(sodium carboxylate) type surfactants (**III**) derived from ethyl tartrate. The biodegradation rate of both **IIIa** and **IIIb** is slow at the early stage. Compound **IIIa** is especially slow, showing a lag time of five days, but on and after the ninth day, the degradability of both compounds increases rapidly. The surfactant **IIIa**, with a proton at position 2 in the ring, shows a 15% higher degradability than **IIIb**, bearing a methyl group at position 2, after fourteen days. The lipophilic group of **IIIb** is apparently branched-chain. Chain branching of the lipophilic group in a surfactant is known to have inhibitory effects on some microorganisms (19). Therefore, it should be reasonable that the biodegradability of **IIIb** is greater than that of **IIIa**.

The surfactants **I**, **II**, and **III** decompose into nonsurface-active species under acidic conditions (7–9). The resultant water-insoluble products are 1-*O*-alkylglycerols (in the case of **I**) or 1,2-alkanediol (in the case of **II**) (Scheme 2). In this work, the biodegradability of 1-*O*-dodecylglycerol (**IV**) and 1,2-dodecanediol (**V**) was also measured under the same conditions (Fig. 4). The degradability of both compounds is high compared with that of sodium dodecanoate. The biodegrad-

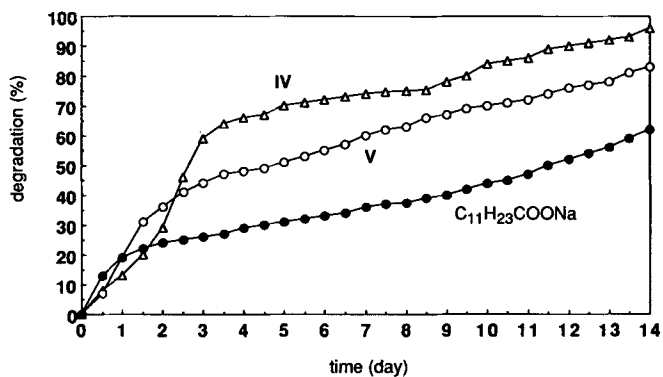
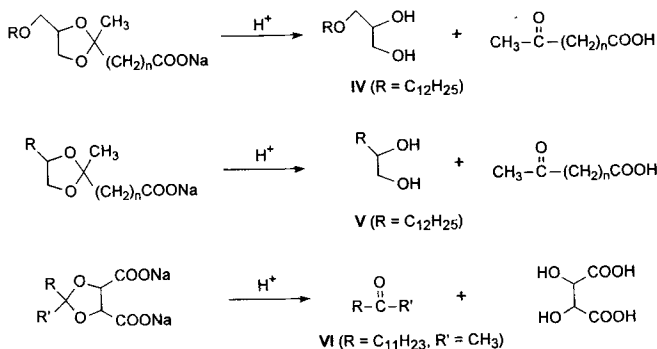


FIG. 4. Biodegradability time course curve for 1-*O*-dodecylglycerol (**IV**), 1,2-dodecanediol (**V**), and sodium dodecanoate.

ability of compound **V** after 14 d is 83%, whereas that of **IV** is about 100%. For **III**, only the biodegradability of 2-tridecanone (**VI**), which is the resultant product of **IIIb**, was measured in this work because aldehydes are easily biodegradable in comparison with the corresponding ketones (20) (Scheme 2). The degradability after 14 d is about 54%, which is almost the same as that of the original surfactant. The lower fatty acids are known to have good biodegradation (20), and thus tartaric acid and all oxocarboxylic acids, which are resultant products of these surfactants (**I–III**), were not measured in this work.

In conclusion, these results show that after fourteen days, the biodegradability of novel carboxylate types of chemocleavable surfactants (**I**, **II**, and **III**) is almost the same as or higher than that of sodium dodecanoate, which is known to be a good biodegradable compound. After fourteen days under the same conditions, the biodegradability of sodium *n*-dodecylbenzenesulfonate (LAS), which is a popular component in commercial detergents, was 15%. These surfactants have much higher biodegradation than LAS. In addition, when the cleavable surfactants (**I** and **II**) are decomposed under acidic conditions after fulfilling their original functions, the biodegradability of the resultant products is much higher than that of the original surfactants. The ease of preparation of these three types of cleavable surfactants, the positive effect of the 1,3-dioxolane ring on various surface-active properties (7–9), and good biodegradability will make these surfactants possible candidates as active components in future ecological detergents.



SCHEME 2

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