

Syntheses of Tritium Labeled Nonionic Detergents

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Received April 22 1971

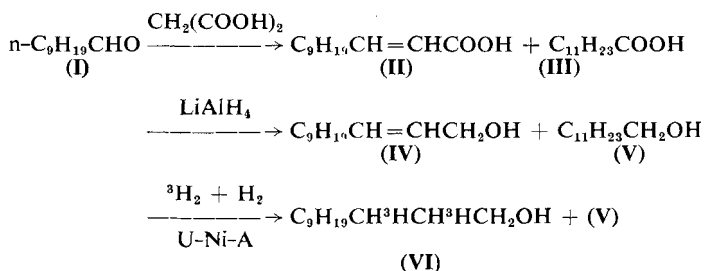
SUMMARY

Tritiated nonionic detergents, tri- and hexaoxyethylene glycol dodecyl ether, have been synthesized by condensation of triethylene glycol and dodecan-2,3-³H, ³H-ol-1, which was obtained by tritiation of 2-dodecenol as the condensation product of decanal and malonic acid. They are found to be chemically, radiochemically and surface-chemically pure enough for adsorption experiments by radiotracer method.

INTRODUCTION.

The radiotracer technique have proved to be effective in elucidating the surface-chemical processes in the bulk and surface phases for ionic detergents labeled with such a radioisotope as ¹⁴C⁽¹⁾, ³⁵S⁽²⁾ or ³H⁽³⁾. For instance, it was confirmed^(4, 5) experimentally that the adsorption of ionic detergent at the air-solution interface obeys to the Gibbs adsorption isotherm⁽⁶⁻⁸⁾. No one, however, has dealt with nonionic detergent for radiometric investigation of its adsorbed amount.

In the present paper, attempts have been made for obtaining tritiated nonionic detergents, such as tri- and hexaoxyethylene dodecyl ether, which are of high purities simultaneously in chemical, surface-chemical and radiochemical criteria. To incorporate tritium atom into organic molecules, various methods⁽⁹⁻¹¹⁾ have been proposed for individual purposes. In the present study, the tritiated amphipathic compounds were conveniently obtained by the following reaction scheme⁽¹²⁾.



After reduction of the mixture of acids, (II) and (III), with LiAlH_4 , the products were found to be the mixture of saturated and unsaturated alcohols in 45 : 54 mole ratio, as is seen in Figure 1. They were identified as n-dodecanol (V) and 2-dodecenol (IV), respectively. The mixture was used for the subsequent tritiation without separating (V) from (IV). Tritiation of (IV) was done with the apparatus⁽³⁾ as shown in Figure 2. Isotopic abundance, $^3\text{H}_2/(^3\text{H}_2 + \text{H}_2)$, of tritium gas used was 98 %.

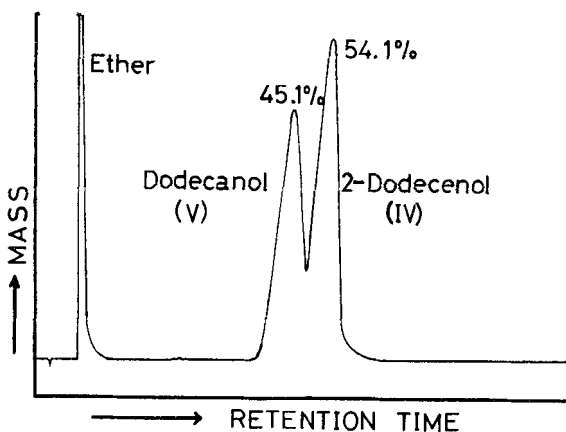
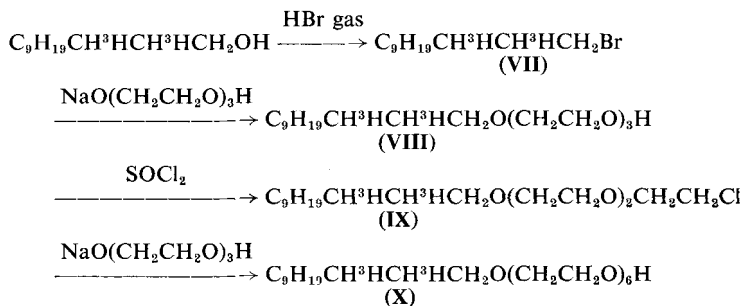


FIG. 1. Gaschromatogram of the reaction, (IV) and (V).
 Stationary phase, 1.5 m PEG-20M at 180° C.
 Carrier gas, 30 ml/min He gas.

After tritiation of the mixed alcohols, the two peaks in Figure 1 were merged to one, that standing for the dodecanol. The absorption of hydrogen gas by (IV) corresponded to what we expected from the area of peak (IV) in Figure 1. The tritiated sample was found to be radiochemically and chemically pure, as is shown in Figure 3.

The tritiated nonionic detergents were synthesized using this tritiated dodecanol *via* the following Williamson's route⁽¹³⁾, with modification in the

brominating method, for which we used dried HBr gas⁽¹⁴⁾, instead of the mixture of aqueous HBr solution and H₂SO₄.



The specific activity of (X) obtained was 21.4 Ci/mole and the radioactive yield was 10.0%. The melting point (25.1°) and the refractive index (n_D^{40} 1.4480) are both in agreement with reported values (24.9° and 1.4479, respectively)

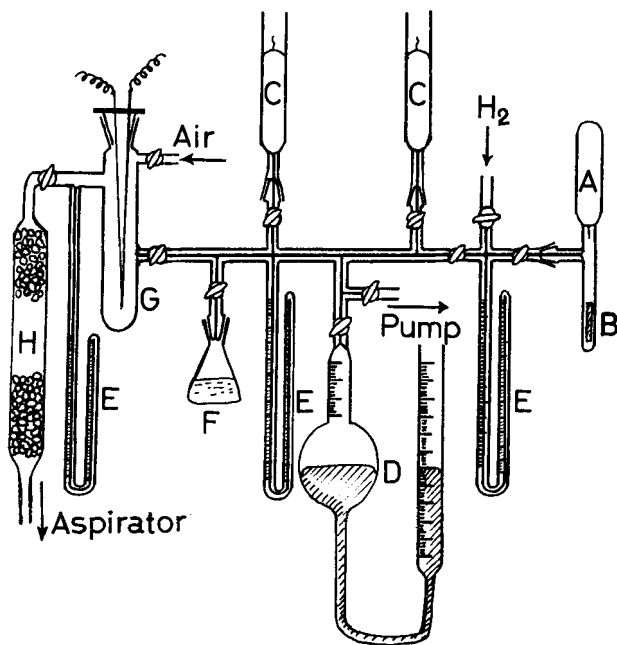


FIG. 2. Tritiation apparatus.

- | | |
|------------------------|---------------------------|
| A Tritium ampoule. | E Manometer |
| B Breaker. | F Reaction flask. |
| C Ampoule for storage. | G Combustion bulb. |
| D Graduated Toepler. | H CaCl ₂ tube. |

for non-radioactive one ⁽¹⁵⁾. The surface-chemical purity was checked by measuring the surface tension of its solution by the drop volume method. As shown in Figure 4, no depression has been found at around the critical micellar concentration (CMC), which agrees to reported values ⁽¹⁶⁾, the fact suggesting the unlikelihood of impurities whose surface-activities are higher than the main component. Also, the sharply broken curve at the CMC indicates that (X) does not contain any other nonionic detergents in homologous series.

It should be noted that the gaschromatograms for the products, (VII), (VIII) and (IX), gave always only one peak for any of them.

EXPERIMENTAL.

Materials.

All organic compounds were further purified by fractional distillation. Urushibara nickel ⁽¹⁷⁾ was produced by treating the mixture of zinc powder and nickel chloride with acetic acid solution. Commercial triethylene glycol was purified carefully by fractional distillation in vacuo under nitrogen gas. Reactions were always achieved under the flowing of dry nitrogen.

2-dodecenoic acid (II).

About 1.23 moles of malonic acid ⁽¹⁸⁾ and 0.47 moles of n-decylaldehyde were dissolved in 200 ml of pyridine under shaking and slightly warming. Piperidine (8 ml) as a catalyst was added to the mixture. The temperature of 80-85° was maintained for 1 hour, and the material was subsequently refluxed (109-115°) for additional 3 hours. After cooling, the reaction mixture was poured into a sufficient volume of water and acidified with 400 ml of concentrated hydrochloric acid. The ethereal extract of the upper layer was washed with water and 5% sodium carbonate solution. The fractional distillation of residue gave 74.4 g (b.p. 146°/3 mm Hg) of (II) in 80% yield.

2-dodecenol (IV).

An ethereal solution of 0.3 moles of (II) was added to a solution of 10 g of LiAlH₄ ⁽¹⁹⁾ in 550 ml of ether at such a rate as to produce gentle reflux. After the completion of the reaction, water was added cautiously to decompose excess hydride. Then, 220 ml of 10% sulfuric acid was added to make the solution clear. The product was purified by fractional distillation (b.p. 103°/2.5 mm Hg) to obtain 29.2 g of (IV) in 52.5% yield.

Dodecan-2,3-³H, ³H-ol-1 (VI).

After evacuation of the apparatus in Figure 2, tritium gas was introduced into F containing 19.5 g of (IV), cyclohexane and Urushibara-nickel-A. After

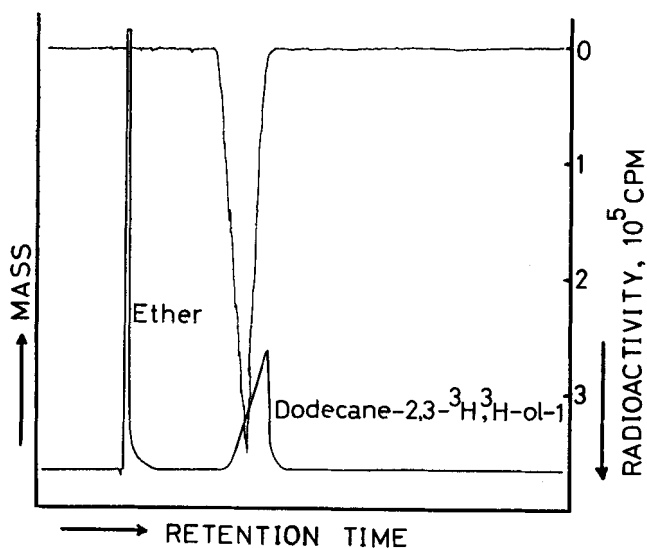


FIG. 3. Radiogaschromatogram of *Dodecan-2,3-³H,³H-ol-1* (VI).
Stationary phase, 1.2 m SE-30 at 159° C.
Carrier gas, 30 ml/min He gas.

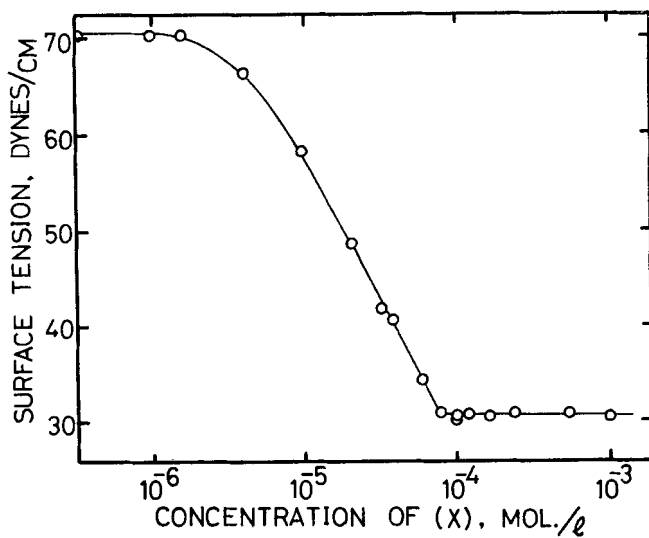


FIG. 4. Concentration dependence of surface tension of tritiated hexaoxyethylene glycol dodecyl ether (X) solution at 30 ± 0.5° C. Surface tension determined by the drop weight method.

saturation of the gas absorption, 10% HCl solution was added to decompose the catalyst. The cyclohexane solution was separated, washed with water and dried with MgSO_4 . 17.0 g of (VI), b.p. 102.6-103°/2 mm Hg, was obtained. The yield was 88%.

Dodecan-2,3-³H, ³H-bromide (VII).

17.0 g of (VI) was heated to 100°⁽²⁰⁾ for melting, and dry hydrogen-bromide was passed in at 100-120° until no more absorption occurred. The crude bromide was separated from the aqueous hydrobromic acid, and shaken with one-third its volume of concentrated sulfuric acid to remove the unreacted dodecanol. The lower bromide layer was washed with an equal volume of 50% methyl alcohol, dried with calcium chloride, and distilled, 105-106.2°/3 mm Hg. 19.7 g of (VII) was obtained. The yield was 87%.

Tritiated trioxyethylene glycol dodecyl ether (VIII).

Sodium (1.75 g) was dissolved slowly at a temperature not exceeding 50° in redistilled triethylene glycol (45 g) under stirring. A portion of 18.9 g of (VII) was added, and stirring continued at 200° until the reaction mixture was neutral (4 hours). After cooling, it was extracted with ether (3 × 150 ml) and the residue, after evaporation of the ether, was re-extracted with warm dry light petroleum (b.p. 60-80°, 3 × 50 ml). These procedures enabled to remove the unreacted glycol present in the original extract. 17.5 g of (VIII) was obtained, b.p. 197°/3 mm Hg; yield, 72.3%.

Tritiated monochloro-trioxyethylene glycol dodecyl ether (IX).

To a mixture of 17.0 g of (VIII) and 4.4 g of pyridine, thionyl chloride (13.3 g) was added dropwise to reflux for 1.5 hour. After decomposing excess of thionyl chloride with water (9 ml), the products were extracted with ligroin. The organic layer was washed with 5% sodium hydrogen carbonate solution and with water, dried with MgSO_4 , and distilled to give 16.7 g of (IX), b.p. 184°/3 mm Hg. The yield was 94.5%.

Tritiated hexaoxyethylene glycol dodecyl ether (X).

A mixture of 16.0 g of (IX) and equivalent amount of trioxyethylene monoalcoholate was heated at 200° for several hours and dissolved in 300 ml of ligroin. Unreacted triethylene glycol was extracted with water at 70°. Other unchanged materials were distilled to remove as lower boiling portions (below 200°/2 mm Hg). The residue (X) was recrystallized three times from cyclohexane, and chromatographed on neutral alumina using a 25 : 24 : 1 acetone : benzene : methanol solvent system. 4.2 g of (X) was obtained. The yield was 19.2%.

The authors thank Professor T. Sasaki for his encouragement and guidance throughout the experiments. They are grateful also to Professor M. Muramatsu, for his helpful advice.

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