

# Synthesis of New Extended Surfactants Containing a Carboxylate or Sulfate Polar Group

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**ABSTRACT:** New extended anionic surfactants with a carboxylate or sulfate polar head were synthesized from polypropoxylated alcohols, and their structures were confirmed by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance analysis. The extended surfactant critical micelle concentration was found to decrease with the length of the polypropylene glycol spacer. Surfactants containing a diethylene glycol link to the head group exhibited a higher critical micelle concentration than did their nondiethoxylated homologs.

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A novel family of surfactants has recently been reported (1–5), that has a structural feature not found in the classic amphiphilic substances. In these so-called extended surfactants, the polar group and the hydrophobic tail are separated by a polypropylene glycol link, sometimes completed by a few polyethylene glycol units close to the head group. The intermediate polarity extension in the middle of the molecule provides a smoother change from a polar to an apolar medium in a way that mimics the so-called lipophilic and hydrophilic linker effects (6–10). As discussed elsewhere (6,7), the lipophilic linker effect induces some organization in the oil layer near the interface, a feature that increases the solubilization of high molecular weight hydrocarbons and polar oils such as triglycerides in alcohol-free microemulsion systems (1). The interest in these compounds is related to their potential applications to a variety of formulations ranging from cosmetic and pharmaceutical products to “green” drilling fluids and water-based cleaners.

There is evidence that the length of the polypropylene glycol spacer arm significantly affects the surfactant properties (1,3–5,11), so different extensions with an average of 6, 10, or 14 propylene oxide units were used in combination with a sulfate or carboxylate sodium salt polar head, eventually con-

nected to the polypropylene glycol with a diethylene glycol link.

We report the synthesis of eight extended anionic surfactants. Scheme 1 shows the synthetic route to the target compounds, starting from the synthetic intermediate, 2-*O*-dodecyl-( $\alpha$ -polypropyleneglycol), the so-called “alcohol-4,” which was prepared according to a method reported previously (4,5).

## EXPERIMENTAL PROCEDURES

**Materials.** Methanesulfonyl chloride, *n*-dodecyl bromide, sodium salt of chloroacetic acid, and polypropylene glycol ( $\bar{M}_n = 425, \bar{M}_n = 725, \bar{M}_n = 1000$ ) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Chlorosulfonic acid was obtained from Merck Chemical Co. (Darmstadt, Germany). Other reagents and solvents were of commercial grade and were not purified before use. The synthesis of compounds 1a, 1b, and 1c was described by Scorzza *et al.* (4,5). Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance 400 MHz instrument (Bruker, Karlsruhe, Germany) for solutions in CDCl<sub>3</sub>, D<sub>2</sub>O, or dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>).

**Synthesis of 2-*O*-dodecyl-1-*O*-ester sodium sulfate-( $\alpha$ -polypropylene glycol 425) (2a).** Compound 1a ( $\bar{M}_n = 593$ , 4.15 g, 7 mmol) and sodium carbonate (1.48 g, 14 mmol) were dissolved in carbon tetrachloride (40 mL). Chlorosulfonic acid (1.63 g, 14 mmol) was added dropwise as the mixture was stirred at 0°C. The reaction was monitored by thin-layer chromatography (TLC) until 1a disappeared, which was after about 8 h. The reaction mixture was neutralized with a 10 N alcoholic sodium hydroxide solution. Solvents were then evaporated under reduced pressure. The product, 2a, was obtained pure as a viscous liquid (5.4 g, 81% yield) on treatment over a silica-gel column with elution using ethyl acetate/methanol (90:10, vol/vol). The NMR data for compound 2a are summarized in Table 1.

**Synthesis of 2-*O*-dodecyl-1-*O*-ester sodium sulfate-( $\alpha$ -polypropylene glycol 725) (2b).** Compound 1b ( $\bar{M}_n = 893$ , 4.47 g, 5 mmol), was treated with sodium carbonate and chlorosulfonic acid in a carbon tetrachloride solution in a fashion similar to that described for the synthesis of 2a to obtain 4.7 g (82% yield) of 2b as a viscous liquid. NMR data are shown in Table 1.

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Abbreviations: alcohol-4, 2-*O*-dodecyl-( $\alpha$ -polypropylene glycol); CMC, critical micelle concentration; DMSO, dimethyl sulfoxide; NMR, nuclear magnetic resonance; TLC, thin-layer chromatography.