

SYNTHESIS OF ^{14}C -LABELLED PROPANESULPHONATES -
APPLICATION TO SURFACTANTS AND HYDROPHILIC POLYMERS

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SUMMARY

1,3-[2- ^{14}C]Propanesultone was identified as a versatile reagent for the preparation of a wide range of ^{14}C -labelled surfactant and hydrophilic polymer propanesulphonates in a convenient, efficient, one-step reaction. A surfactant, sodium dinonylphenylhexaethoxy[2- ^{14}C]propanesulphonate was prepared by the reaction of the corresponding ethoxyalcohol with 1,3-[2- ^{14}C]propanesultone in xylene at 140° for 2.5h using sodium hydride as base. Conversion, as measured by High Performance Liquid Chromatography, was 77%. Pure sulphonate was obtained after silica gel column chromatography at specific activity 31.5 $\mu\text{Ci/g}$ in 52% yield. Structure was confirmed by ^1H and ^{13}C NMR spectroscopy. A low molecular weight hydrophilic polymer sulphonate has been prepared in radiolabelled form by the reaction of poly(vinylalcohol) MW 14,000 with 1,3-[2- ^{14}C]propanesultone in dimethylsulphoxide with potassium carbonate as base at 85° for 18h. The ^{14}C -labelled poly(vinylalcohol) potassium propanesulphonate so formed had specific activity 8.0 $\mu\text{Ci/g}$ and was obtained in 96% yield. The degree of propanesulphonation of polymer was 19.5%.

Key Words: ^{14}C -Polymer Sulphonate, 1,3-[2- ^{14}C]Propanesultone, ^{14}C -Surfactant, Sulphonation.

INTRODUCTION

Accurate and sensitive methods for the determination of low levels of surfactants are indispensable for a variety of research programmes such as the study of surfactant biodegradation, the study of the metabolism of surfactants for food use and the identification of surfactant systems

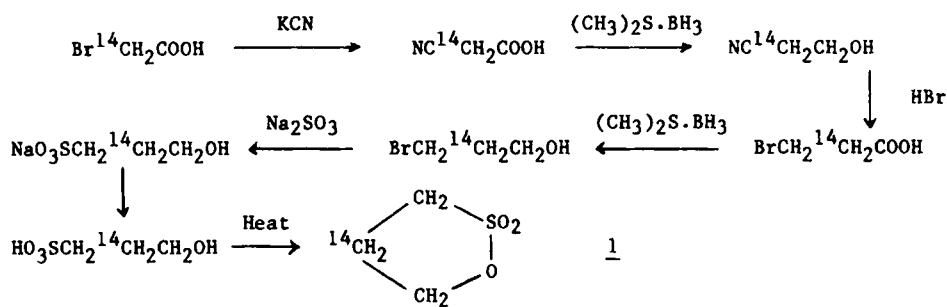
for use in an enhanced oil recovery flood process. The most suitable analytical tool for monitoring surfactant concentrations in these situations involves the determination of radiolabelled surfactants and this publication describes the preparation of a particular class of surfactant incorporating ^{14}C from a single reagent. Furthermore, the methods employed are suitable for the synthesis of a wide variety of ^{14}C -labelled propanesulphonates and this will be exemplified by the preparation of a low molecular weight hydrophilic polymer propanesulphonate.

The preparation of radiolabelled surfactants is widely documented in the literature. Such synthetic work has usually formed part of a study of surfactant biodegradation. The synthesis of radiolabelled ethoxylated octadecanol and dodecanol with ^{14}C in the alkyl group or polyoxyethylene chain has recently been reported (1). Doubly radiolabelled alkylphenyl-ethoxyalcohols and alkylethoxyalcohols have been employed (2) to provide an in-depth understanding of the biodegradation of these important classes of surfactants. Tritium (^3H) was incorporated into the benzene ring or alkyl group and ^{14}C was incorporated into the polyoxyethylene chain for this study. Radiolabelling of an alkylethoxysulphate has been achieved by the incorporation of ^{35}S (3). Thus, sulphation of dodecyltrioxyethylene-alcohol with [^{35}S]sulphuric acid gave the radiolabelled sulphate for biodegradation studies. Sodium dodecylbenzenesulphonate has been prepared with ^{14}C -labelling in the benzene ring by a three-step synthetic procedure starting from [^{14}C]benzene (4). The manipulation of radiolabelled material over a long reaction sequence is to be avoided where possible, however, and a radiochemical yield of only 25% was achieved in this instance.

RESULTS AND DISCUSSION

Surprisingly, literature procedures for the preparation of radiolabelled propanesulphonate surfactants are not available. Propanesulphonate

surfactant series such as alkyl/alkylphenylethoxypropanesulphonates are commercially available and have recently been patented as single-component surfactants for secondary water flooding or tertiary oil recovery (5). It was decided that radiolabelled surfactants of these classes could most economically and efficiently be prepared by introducing the radiolabel in the last stage of their syntheses, the alkanesulphonation step, by the use of a single radiolabelled reagent that could be applied in a wide variety of cases. ¹⁴C-Labelled 1,3-propanesultone was the reagent of choice as it could be applied to the synthesis of a range of propanesulphonate surfactants in a single step. In addition, propanesulphonation can be achieved routinely to an extent of greater than 90% so that wastage of expensive radiolabelled reagent would be small. 1,3-[2-¹⁴C]Propanesultone 1 at specific activity 7.1 μ Ci/mg was prepared by Amersham International plc from bromo[2-¹⁴C]acetic acid by a seven stage sequence given in the Reaction Scheme.

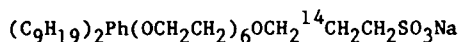


Reaction Scheme

The 1,3-[2-¹⁴C]propanesultone was supplied as a liquid in a glass ampoule. Radiochemical purity was greater than 95% by Thin Layer Chromatography and the infrared spectrum was consistent with structure.

A ¹⁴C-labelled surfactant, sodium dinonylphenylhexaethoxy[2-¹⁴C]-propanesulphonate 2, was prepared by the reaction of dinonylphenylhexa-

ethoxyalcohol with 1,3-[2-¹⁴C]propanesultone 1. The sultone (specific activity 7.1 $\mu\text{Ci}/\text{mg}$)



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was diluted with freshly distilled unlabelled 1,3-propanesultone to provide reagent of specific activity 194 $\mu\text{Ci}/\text{g}$. Dinonylphenylhexaethoxyalcohol was reacted with 1.2 equivalents of sodium hydride in xylene and the ethoxylate anion produced was heated at 140° with one equivalent of the diluted 1,3-[2-¹⁴C]propanesultone for 2.5h. Crude reaction product was analysed by High Performance Liquid Chromatography which indicated a 77% molar conversion of nonionic to anionic. The term nonionic here and subsequently refers to the family of dinonylphenylethoxyalcohols of different ethoxy chain lengths which are the major components of the commercial surfactant product used as starting material for this reaction. Similarly the term anionic refers to the mixture of propanesulphonates derived from the dinonylphenylethoxyalcohols. This less than quantitative conversion is due to the presence of polyethyleneglycols (up to 10%) in the ethoxyalcohol which are generated as by-product when alkylphenols are reacted with ethylene oxide using potassium hydroxide as catalyst. The as-made propanesulphonate surfactant was purified to 100% anionic 2 by column chromatography on silica gel using chloroform-methanol gradient elution. Pure 2 was obtained as a colourless oil in 52% yield by weight. Specific activity was 31.5 $\mu\text{Ci}/\text{g}$ and High Performance Liquid Chromatography indicated that the material was anionically pure. ¹H and ¹³C NMR spectra were consistent with structure and ¹H NMR indicated an average ethoxy value of 6.5 for surfactant 2. It is anticipated that this simple sulphonation procedure could be applied to a wide variety of alkyl and alkylphenylalkoxyalcohols for the synthesis of ¹⁴C-labelled surfactants similar to 2.

The generality of this procedure for preparing ¹⁴C-labelled propanesulphonates of alcohols was then illustrated by the synthesis of poly(vinylalcohol) MW 14,000 potassium propanesulphonated to an extent of 18%, a water soluble, low molecular weight, sulphonate polymer. Potassium carbonate (6) and sodium hydride (7) have been used as the base in the reaction of poly(vinylalcohol) with 1,3-propanesultone both with excellent results. It was decided to follow the simpler potassium carbonate procedure in the radiolabelling synthesis. The 1,3-[2-¹⁴C]propanesultone at specific activity 194 μCi/g from the first dilution was further diluted with freshly distilled unlabelled 1,3-propanesultone to provide reagent of specific activity 39.8 μCi/g. This was reacted with poly(vinylalcohol) MW 14,000 in the presence of potassium carbonate in anhydrous dimethylsulphoxide at 85° for 18h (6). These conditions have been reported (6) to effect a degree of potassium propanesulphonation of 18%. In this reaction approximately 50% of the 1,3-propanesultone used combines irreversibly with the dimethylsulphoxide solvent and consequently is not available for reaction with poly(vinylalcohol). It was calculated that the procedure employed would yield polymer with specific activity 12.8 μCi/g. Pure ¹⁴C-labelled poly(vinylalcohol) potassium propanesulphonate (7.5g) was obtained as an off-white fibrous solid in 96% yield based on the poly(vinylalcohol). The degree of propanesulphonation was 19.5% as determined by combustion microanalysis of sulphur. Specific activity was 8.0 μCi/g.

This simple radiolabelling technique is available for application to the synthesis of other propanesulphonates of low molecular weight hydroxylic polymers such as polyacrylates and polysaccharides.

EXPERIMENTAL

1,3-[2-¹⁴C]Propanesultone was purchased from Amersham International plc; dinonylphenylhexaethoxyalcohol was supplied by Tensia; 1,3-propane-

sultone was purchased from Aldrich; poly(vinylalcohol), sodium hydride, dimethylsulphoxide and acetone were purchased from BDH; potassium carbonate and xylene were purchased from Fisons. High Performance Liquid Chromatography was performed with a Waters Associates Model 6000A Solvent Delivery System and RCM-100 Radial Compression Module with 8 mm ID reverse-phase C₁₈ cartridge. The solvent system was 4:1 isopropanol:water with 0.2% phosphoric acid. Detection was performed with a Cecil CE 2112 variable wavelength ultraviolet monitor (at 254 nm) and a Hewlett-Packard Model 3390A Reporting Integrator was used to record and integrate the trace. ¹H and ¹³C NMR Spectra were recorded on a Jeol FX 270 spectrometer at 270 and 67.78 MHz respectively in CDCl₃ solutions. Chemical shifts are reported as values (ppm downfield from TMS).

Sodium Dinonylphenylhexaethoxy[2-¹⁴C]propanesulphonate 2

Dinonylphenylhexaethoxyalcohol (5.15g, 8.44 mM) was dissolved in xylene (40 ml) and the solution was dried by Dean-Stark distillation with the removal of 20 ml xylene. A low throughput of dry nitrogen was then applied over the solution. Sodium hydride (80% dispersion in oil, 0.3g, 10.1 mM, 1.2E) was added portionwise to the solution at room temperature as a slurry in anhydrous xylene (10 ml). The oil was initially removed from the sodium hydride by washing with anhydrous xylene (5 ml) followed by decantation of the xylene. The solution was heated at 100° for 1h. Effervescence had ceased after this time.

1,3-[2-¹⁴C]Propanesultone 1 (0.143g, 1 mCi) was washed into a volumetric flask containing unlabelled 1,3-propanesultone (5.007g) and the solution was made up to 100 ml with anhydrous xylene. A 20 ml aliquot containing diluted 1,3-[2-¹⁴C]propanesultone 1 (1.03g, 200 μCi, 8.44 mM, 1E) was added to the reaction mixture which was then heated at 140° for 2.5h. The solution was allowed to cool to 50° and water (0.5 ml) was added. The mixture was then heated to 100° for 0.3h. Solvent was evaporated

and the red oily residue was pumped at 0.4 mm/60° for 15h. Crude propane-sulphonate (6.53g) was obtained of specific activity 28.9 μCi/g and 77% conversion of nonionic to anionic as determined by High Performance Liquid Chromatography. The reaction product was purified by column chromatography on silica gel (110g) using chloroform-methanol gradient elution. Pure anionic 2 was obtained as a colourless oil (3.3g) after pumping at 2 mm/50° for 3h. Recovery of material from the column was 67% and overall yield based on alcohol precursor was 52%. Specific activity was 31.5 μCi/g. Product was pure anionic by High Performance Liquid Chromatography. ¹H NMR : 0.38-1.90 (m, 38H, 2C₉H₁₉), 2.06 (quintet, J=6 Hz, 2H, CH₂CH₂SO₃Na), 3.00 (m, 2H, CH₂SO₃Na), 3.43-4.08 (m, 28H, OCH₂CH₂O and OCH₂CH₂CH₂), 6.66-7.28 (m, 3H, ArH); ¹³C NMR : 4.9-43.2 (m, 18C, 2C₉H₁₉), 24.8 (s, 1C, CH₂CH₂SO₃Na), 48.0 (s, 1C, CH₂SO₃Na), 66.2-70.6 (m, 14C, OCH₂CH₂O and OCH₂CH₂CH₂), 110.0-155.9 (m, 6C, ArC).

Poly(vinylalcohol) Potassium Propanesulphonated to 19.5%

Poly(vinylalcohol) (4.55g, 0.103M of repeat unit, MW 14,000) was dissolved in anhydrous dimethylsulphoxide (114 ml) and the solution was heated to 85°. Anhydrous potassium carbonate (2.89g, 0.021M) was added in one portion. A 20 ml aliquot of the diluted solution of 1,3-[2-¹⁴C]-propanesultone (1.03g, 200 μCi) prepared previously in xylene was added to unlabelled 1,3-propanesultone (4g) and the resulting solution was evaporated to dryness. The resultant radiolabelled 1,3-propanesultone (5.03g, 200 μCi, 0.041M, 2E) was dissolved in anhydrous dimethylsulphoxide (23 ml) and the solution was added in one portion to the heated reaction mixture directly after the potassium carbonate. The mixture was stirred mechanically at 85° for 18h. The red solution was allowed to cool to room temperature and was then added dropwise over 0.25h to mechanically stirred ethanol (95%, 500 ml). The yellow precipitate was filtered off

and was washed with ethanol (95%, 1 l). The solid was dissolved in the minimum volume of water and the solution was added dropwise over 1h to mechanically stirred acetone (2.5 l). The cloudy solution was decanted from the off-white, fibrous residue. The latter was washed with acetone (2 x 250 ml) and solvent was decanted. Solid product was dried in vacuo at 0.6 mm/50° for 8h. The ¹⁴C-labelled poly(vinylalcohol) potassium propanesulphonate was obtained as an off-white, fibrous solid (7.5g) in 96% yield based on poly(vinylalcohol). Gas-Liquid Chromatography indicated a dimethylsulphoxide level of less than 350 ppm. Combustion microanalysis of sulphur indicated a degree of propanesulphonation of 19.5%. Specific activity was 8.0 μ Ci/g.

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