# Lactose-derived Surfactants (III): Fatty Esters of Oxyalkylated Lactitol

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## ABSTRACT AND SUMMARY

Lactitol was oxyalkylated with propylene or ethylene oxide. The resulting ether-alcohols were transesterified with a series of fatty acid esters in order to produce long chain ether-esters of lactitol. These compounds were found to be more water soluble than related lactitol derivatives prepared by transesterification prior to oxyalkylation. Improved lime soap dispersant requirements (LSDR) and emulsification times were obtained from the new derivatives.

## INTRODUCTION

Previous research in this laboratory has indicated that lactose can be esterified by acylation with fatty acyl halides (1) and that its reduction product, lactitol, can be transesterified with fatty acid esters (2). The resulting monoesters were evaluated for their surface-active properties such as detergency behavior, emulsification time, and lime soap dispersant requirement. In addition, oxyethylated derivatives of these esters were also prepared and tested for surface-active properties. The results obtained indicated that lactose-derived surfactants were comparable to similar sucrose derivatives. However, some lactose derivatives were less soluble, and mechanical stirring was necessary in order to achieve complete solution or dispersion of the esters prior to being tested.

We describe the preparation and properties of surfactants obtained by addition of propylene oxide or ethylene oxide to lactitol, followed by transesterification of the resulting ether-alcohols. It was expected that the ether-esters would be somewhat different in structure and properties from the derivatives previously prepared.

## EXPERIMENTAL PROCEDURES

### Materials

Lactitol was obtained from ICI United States, Inc., Wilmington, DE. Methyl laurate, methyl palmitate, methyl stearate, and methyl oleate were prepared from the appropriate purified fatty acids by esterification with methyl alcohol and subsequent distillation. Each of the esters was over 99.3% pure as shown by gas liquid chromatography.

### Procedures

*Oxypropylation of lactitol:* Propylene oxide (PO) was added to lactitol at 130-140 C and atmospheric pressure. The oxide was added dropwise to a stirred solution of lactitol in N-methylpyrrolidone with 4 mole % of potassium hydroxide as catalyst. The solution was periodically weighed after gently bubbling a stream of nitrogen through the mixture to remove unreacted oxide. Addition was continued until 10 moles of PO per mole of lactitol had been taken up. Thin layer chromatography (TLC) showed that the product contained no unreacted lactitol. Portions of the resulting solution were used in subsequent transesterifications.

*Oxyethylation of lactitol:* Addition of ethylene oxide (EO) to lactitol was carried out in a stainless steel autoclave containing 34.4 g (0.10 mole) lactitol dissolved in 250 ml N-methylpyrrolidone and 0.22 g (0.004 mole) potassium hydroxide. Forty-four grams (1.0 mole) of liquified EO were added to the reaction vessel, which was then sealed, and the mixture was stirred magnetically while being heated at 140 C for 2 hr. At that time the reaction was complete since there was no further pressure drop. The autoclave was cooled to room temperature, and the solvent was removed under reduced pressure. The addition of 1.0 mole of EO was confirmed by weight gain, and TLC showed that all of the lactitol had reacted. The ether-alcohol was redissolved in N,N-dimethyl formamide (DMF), and portions of the solution were used in subsequent reactions.

*TLC of oxyalkylated lactitol:* Commercial (Analtech Uniplates) TLC plates of silica gel (250 μ thickness) were spotted with 1% solutions of the oxyalkylated lactitol in N-methylpyrrolidone or dimethyl formamide (DMF) and with a 1% solution of lactitol in DMF. The plates were air-dried and developed with a solvent system of 85% chloroform and 15% methyl alcohol. After being air-dried, the plates were exposed to iodine vapor to reveal their components. It was readily apparent that the lactitol remained at the origin while the less polar oxyalkylated derivatives could be detected as several overlapping zones at the top of the plate. The oxyalkylated products contained no lactitol.

*Transesterifications of oxyalkylated lactitol:* An equimolar amount of the appropriate fatty methyl ester was added to a portion of the PO or EO adduct dissolved in DMF and containing a catalytic amount of potassium tertiary butoxide. The reaction vessel was equipped with a distilling head and condenser and was heated at 80 C under reduced (50 mm) pressure for 24 hr. The solvent was then removed by distillation, and the residue was extracted several times with petroleum ether to remove any unreacted methyl ester. The latter usually approximated 20-25% of the original. The products were not purified further for subsequent measurements of surface-active properties. TLC indicated that the products were different from the lactitol ester-EO adducts prepared previously (2).

*Surface-active properties:* Detergency measurements were carried out as previously described (1) with EMPA (cotton), Testfabrics (cotton-polyester with permanent press finish), and U.S. Testing (cotton) cloths. Again, 0.10 and 0.02% concentrations of the esters were used in two water hardnesses (50 and 300 ppm) with Triton X-100 (Rohm and Haas Company, Philadelphia, PA) as a standard. Results (Table I) are given in terms of reflectance differences (ΔR) before and after washing. Emulsion stabilities were measured by standard means (1) in an Atlab Emulsion Test Apparatus, and lime soap dispersant requirements (LSDR) were determined by the Borghetty and Bergman method (3). Results are summarized in Table II.

## RESULTS AND DISCUSSION

The ether-esters described are undoubtedly complex mixtures formed during the oxyalkylation and transesterification steps. Oxyalkylation with 10 moles of PO or EO

TABLE I

Detergency Data ($\Delta R$)[a] Esters of Oxyalkylated Lactitol

| Compounds and concentrations | | Testfabrics | | EMPA | | U.S. Testing | |
|---|---|---|---|---|---|---|---|
| | | 300 ppm $H_2O$ | 50 ppm $H_2O$ | 300 ppm $H_2O$ | 50 ppm $H_2O$ | 300 ppm $H_2O$ | 50 ppm $H_2O$ |
| EO[b]-Laurate | (0.1%) | 18.4 | 19.0 | 8.0 | 10.6 | 7.6 | 7.6 |
| | (0.02%) | 7.0 | 8.6 | 4.5 | 6.5 | 1.6 | 2.6 |
| PO[c]-Laurate | (0.1%) | 15.0 | 18.8 | 7.3 | 9.1 | 0.1 | 3.8 |
| | (0.02% | 9.0 | 9.5 | 5.9 | 8.7 | 0.0 | 3.1 |
| EO-Palmitate | (0.1%) | 15.8 | 12.9 | 8.5 | 10.8 | 5.6 | 5.6 |
| | (0.02%) | 10.5 | 11.6 | 7.5 | 9.5 | 3.6 | 3.6 |
| PO-Palmitate | (0.1%) | 17.7 | 21.1 | 6.9 | 9.2 | 4.7 | 6.0 |
| | (0.02%) | 12.8 | 10.9 | 5.9 | 9.1 | 3.5 | 4.5 |
| EO-Oleate | (0.1%) | 12.8 | 12.2 | 8.6 | 11.6 | 4.6 | 4.6 |
| | (0.02%) | 11.3 | 9.9 | 7.9 | 8.5 | 3.6 | 3.6 |
| PO-Oleate | (0.1%) | 22.8 | 23.4 | 5.9 | 9.5 | 12.3 | 12.0 |
| | (0.02%) | 14.7 | 12.8 | 6.3 | 8.4 | 5.5 | 4.1 |
| EO-Stearate | (0.1%) | 13.6 | 12.4 | 8.5 | 11.2 | 5.6 | 5.6 |
| | (0.02%) | 11.6 | 11.4 | 8.5 | 10.5 | 4.6 | 3.6 |
| PO-Stearate | (0.1%) | 19.0 | 18.0 | 7.6 | 9.3 | 6.3 | 7.1 |
| | (0.02%) | 12.7 | 10.9 | 5.6 | 8.1 | 4.0 | 4.1 |
| Standard[d] | (0.1%) | 25.0 | 23.2 | 7.5 | 12.5 | 9.6 | 12.6 |
| | (0.02%) | 19.7 | 22.6 | 7.9 | 10.5 | 6.6 | 6.6 |

[a] $\Delta R$ = increase in reflectance after washing.
[b] EO = ethylene oxide adduct.
[c] PO = propylene oxide adduct.
[d] Triton X-100.

per mole of lactitol was carried out conventionally in the presence of an alkaline catalyst. Transesterification was carried out initially with a threefold excess of the oxyalkylated lactitol in analogy to the transesterification of sucrose with methyl esters of fatty acids (4). It was found later that transesterification with equimolar quantities of the fatty esters gave products of superior surface-active properties; hence, this became the preferred transesterification procedure. In this way the presence of large amounts of unreacted lactitol ethers in the prepared ether-esters was avoided. Since purification of the resulting esters would not be feasible from a practical point of view, all evaluations reported here were carried out on the crude products. The materials prepared in this study were found to be more readily water-soluble than the lactose-derived surfactants reported previously (1,2). No mechanical agitation was necessary to achieve solution, although it was noted that solubility decreased with increasing size of fatty acid ester.

Table I summarizes the detergency data obtained at surfactant concentrations of 0.1 and 0.02%. As expected, results (as judged by higher $\Delta R$ values) were better at the greater concentration and slightly better when water hardness was 50 ppm rather than 300 ppm. No great difference in detergency was noted between the PO or EO derivatives. As noted in previous publications, the control detergent (Triton X-100) appeared to perform better in washing Testfabrics cloths, but was not superior to our compounds when EMPA or UST fabrics were used. The oxyethylated lactitol esters reported previously (2) and the oxyethylated components of this study show no great differences with respect to detergency.

In general, greater emulsification times were obtained with derivatives containing propylene oxide units incorporated into their structures than with those with oxyethyl groups (Table II). On the other hand, the LSDR values obtained from ethylene oxide-containing esters were superior to those which had been oxypropylated. Apparently the increased lipophilic mass of the oxypropylated esters is beneficial for greater emulsion stability whereas improved lime soap dispersing ability requires an increase in the hydrophilic mass which is furnished by oxyethylation.

TABLE II

Surface-Active Properties of Various Esters of Oxyalkylated Lactitol

| | Atlab emulsification time (sec) | LSDR[d] (%) |
|---|---|---|
| Lactitol-EO[a]-Laurate | 60 | 9 |
| Lactitol-PO[b]-Laurate | 300 | 13 |
| Lactitol-EO-Palmitate | 60 | 12 |
| Lactitol-PO-Palmitate | 55 | 14 |
| Lactitol-EO-Oleate | 110 | 12 |
| Lactitol-PO-Oleate | 320 | 12 |
| Lactitol-EO-Stearate | 240 | 12 |
| Lactitol-PO-Stearate | 270 | 16 |
| Standard[c] | 52 | 4 |

[a] EO = ethylene oxide.
[b] PO = propylene oxide.
[c] Triton X-100.
[d] LSDR = lime soap dispersant requirement.

It is interesting to compare the emulsification and lime soap dispersing properties of the oxyethylated compounds of this study with those reported previously (2), which were prepared by oxyethylation after transesterification of lactitol with fatty esters. The lime soap dispersing properties of the compounds of this study are substantially better, and the emulsifying properties of the laurate are also better. However, the emulsifying properties of the other esters of this study are inferior.

The emulsification times reported in Table II for PO containing esters as well as the low LSDR figures for EO esters are the best reported to date for any seriies of lactose-based surfactants. Also, water solubility of the new derivatives was improved, although no significant improvement in detergency properties was observed.

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