

# Process for Preparing Nonionic Surfactant Sorbitan Fatty Acid Esters with and without Previous Sorbitol Cyclization

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The purpose of this work was to determine the course of the esterification reaction of hexitols and a long chain length fatty acid at different temperatures. Sorbitol esters of lauric acid were prepared by the esterification of sorbitol and lauric acid (molar ratio, 1:1) in the presence of *p*-toluenesulfonic acid as a catalyst. The esterification was carried out at 140, 150, 160, and 180 °C, with and without sorbitol cyclization, under atmospheric pressure. The reaction course was followed by taking samples after 15, 30, 45, 60, 90, 120, and 150 min, and determining the acid value. The results shows that the conversion of lauric acid is better if sorbitol is previously cycled at all examined temperatures. This work presents one possible solution to a problem that should be of interest to surfactant and carbohydrate chemists.

**Keywords:** *Nonionic surfactants; sorbitan fatty acid esters; rate of esterification; color of the esterification product*

## INTRODUCTION

The purpose of this study was to examine the course of the esterification reaction of hexitols and a long-chain fatty acid at different temperatures and to compare the conversions at these temperatures. Sorbitol fatty acid esters (SFAE) are nonionic surfactants (NSEG; Martinenghi, 1963) are obtained from sorbitol and sorbitol mono- and dianhydride with saturated and unsaturated fatty acids with different chain lengths of fatty acid. Sorbitol esters are W/O-type emulsifiers and are in the same category as SFAEs. Compounds of this type can be used as emulsifiers and stabilizers (Turco, 1980) in the food (Schuster, 1985) and cosmetic industries (Hauthal, 1992) because of low toxicity (acceptable daily intake = 0–25 mg/kg/day; Schuster, 1985). Sorbitan esters have steadily grown during the last decades and have become worldwide standard emulsifiers (no. E493) with numerous producers.

Chemically, SFAEs are complex mixtures of fatty acid esters of several polyols derived from sorbitol (Sahasrabudhe and Chadha, 1969). These compounds are prepared by heating sorbitol and fatty acids at 140, 150, 160, and 180 °C in the presence of a catalyst, such as *p*-toluenesulfonic acid (*p*-TSA), with and without previous sorbitol cyclization. The reaction of dehydration (sorbitol cyclization) is carried out for 1 h at 140 °C under atmospheric pressure.

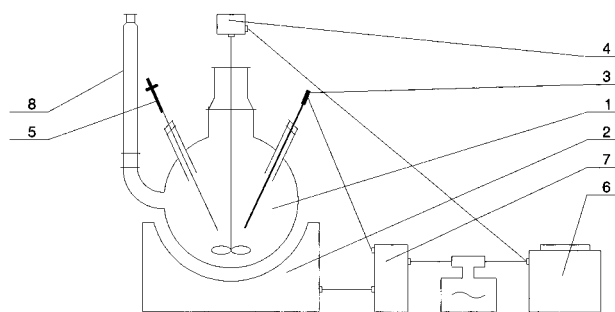
Two of the known polyols, other than sorbitol itself, are its anhydride, 1,4-sorbitan (1,4-anhydro-D-sorbitol) and the dianhydride, 1,4-3,6-isosorbide (1,4:3,6-dianhydro-D-sorbitol). The polyols are esterified, with and without sorbitol cyclization at 140, 150, 160, and 180 °C, with fatty acids, resulting in a complex mixture of mono-, di-, and tri-fatty acids esters.

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**Figure 1.** Esterification apparatus: (1) standard glass apparatus; (2) electric heater; (3) thermometer; (4) stirrer; (5) sampling capillary; (6) sliding control; (7) thermoregulator; and (8) reflux apparatus.

The reaction course was followed by taking samples after 15, 30, 45, 60, 90, 120, and 150 min and determining the acid value. The extent of conversion of acid to sorbitan esters was calculated as mass-% (Giacometti et al., 1995).

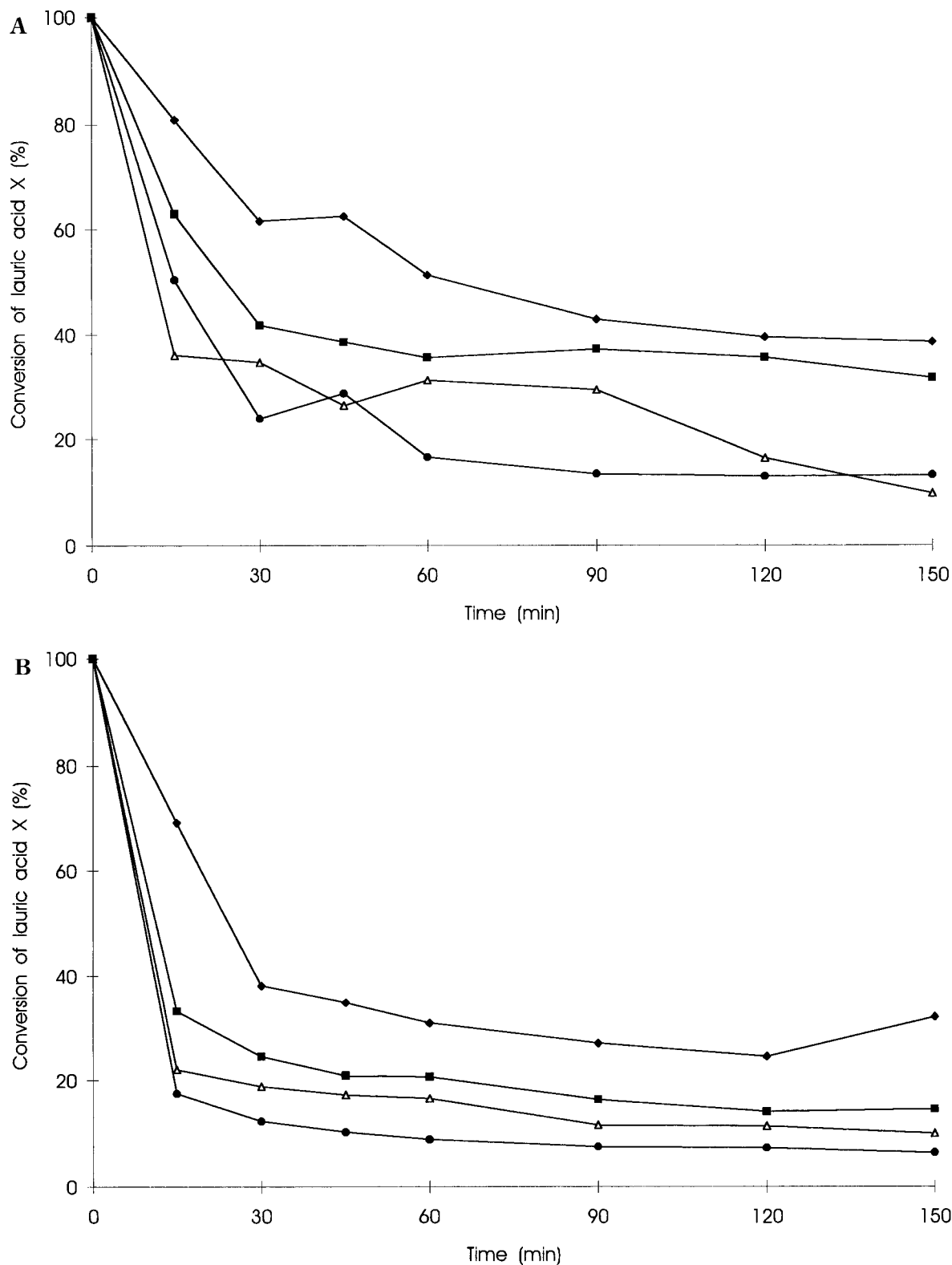
## EXPERIMENTAL PROCEDURES

**Materials.** The following compounds were purchased from commercial sources: lauric acid ( $C_{12}H_{24}O_2$ ), 98% pure (Fluka, Buchs, Switzerland); D-sorbitol ( $C_6H_{14}O_6$ ), 99.5% pure (Hefti, Zurich, Switzerland); *p*-toluenesulfonic acid hydrate ( $CH_3C_6H_4SO_3H \cdot xH_2O$ ) (Carlo Erba, Milan, Italy); 0.1 M KOH-ethanol (Kemika, Zagreb, Croatia); phenolphthalein (Carl Erba, Milan, Italy); and ethanol ( $C_2H_6O$ ) *p.a.* (Kemika, Zagreb, Croatia).

**Preparation of Esters.** The standard glass apparatus where the sorbitol esters were prepared is shown in Figure 1.

Individual fatty acid esters were prepared by two procedures. Sorbitol and lauric acid (1:1, w/w), in the presence 0.1% (w/w) *p*-toluenesulfonic acid as catalyst, were esterified at 140, 150, 160, and 180 °C (method A, without cyclization). The reaction course was followed by taking samples after 15, 30, 45, 60, 90, 120, and 150 min and determining the acid value.

Sorbitol was cyclized with *p*-toluenesulfonic acid (0.1%, w/w) at 140 °C (1 h) and esterified with lauric acid (1:1, w/w) at 140, 150, 160, and 180 °C (method B, with cyclization). The reaction course was followed as in method A.



**Figure 2.** Course of conversion rate at various temperatures determined by (A) method A and (B) method B: (◆) 140 °C; (■) 150 °C; (△) 160 °C; and (●) 180 °C.

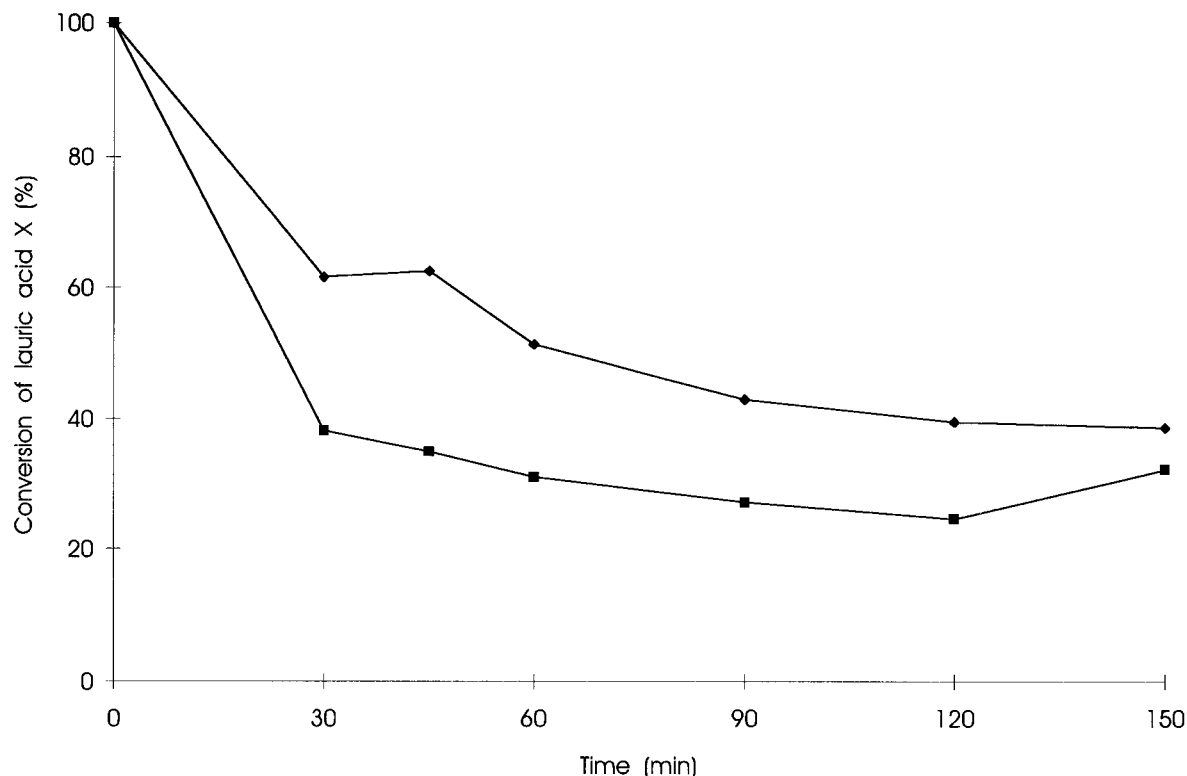
**Conversion of Fatty Acid.** The extent of conversion of acid into sorbitan esters was determined as follows: samples of the reaction mixture were taken periodically during the reaction, and the concentration of the residual fatty acids was determined by titration with 0.1 M KOH–ethanol. The extent of conversion was calculated.

**Color Determination of the Reaction Products.** Color determination of the reaction products was performed with a photometer (Iskra, Kranj, Slovenia, type MA9510) with green filter (wavelength, 540 nm). An equal quantity of samples was

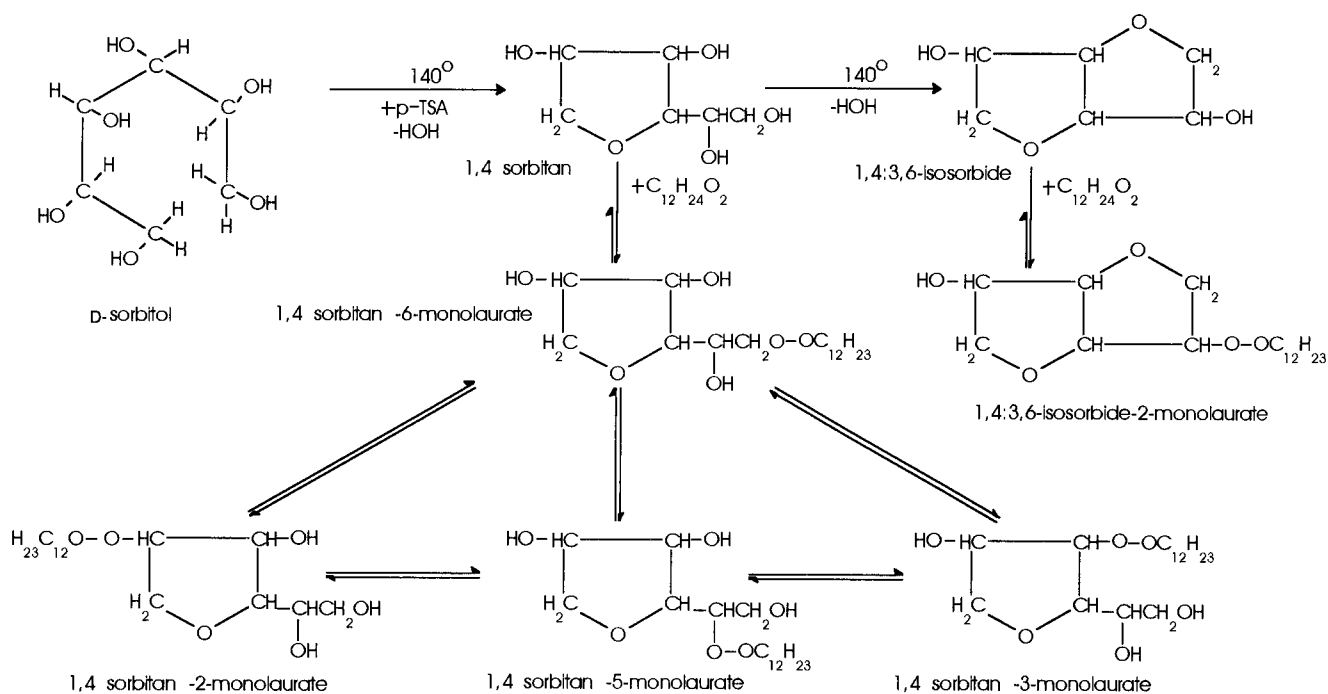
dissolved in an equal quantity of ethanol. The color of esters was determined by taking samples after 150 min at 140, 150, 160, and 180 °C, with and without sorbitol cyclization, and determining absorbance in a beam of monochromatic light entering the solution.

## RESULTS AND DISCUSSION

The purpose of this work was to determine the esterification reaction course of hexitols and a long-



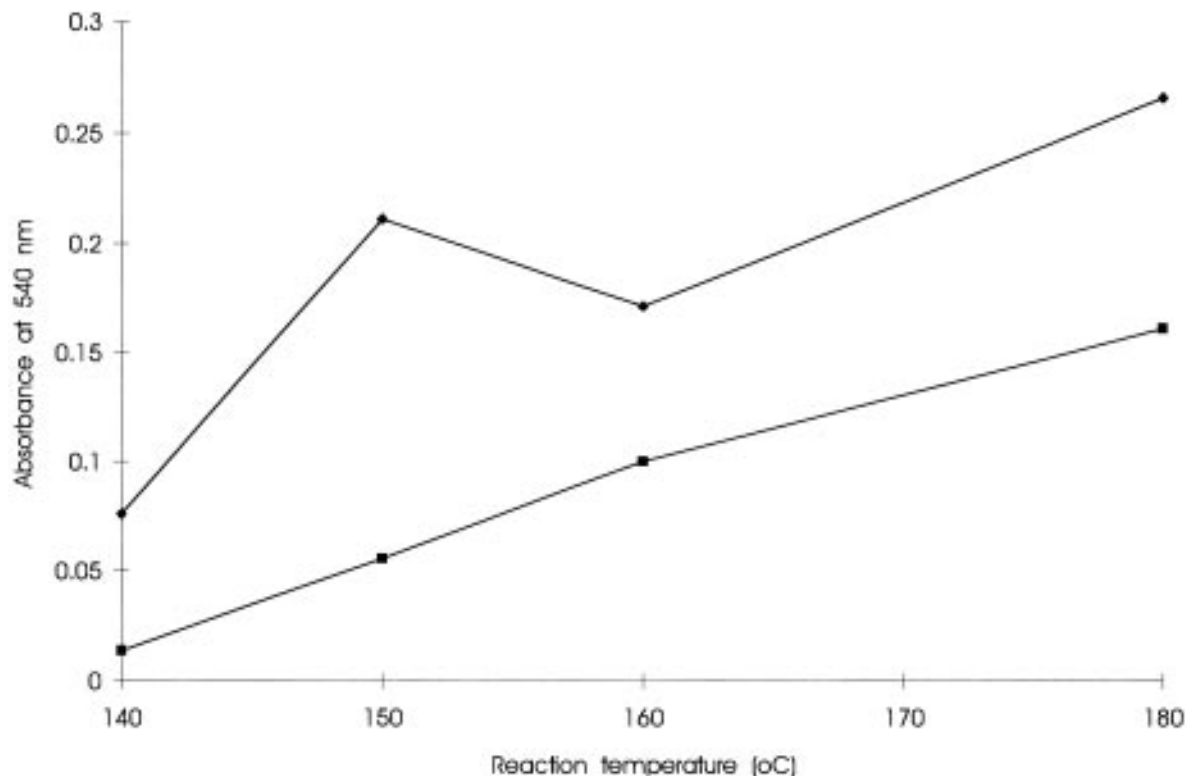
**Figure 3.** Course of conversion rate at 140 °C: (◆) without cyclization; (■) with cyclization.



**Figure 4.** Hypothetical sequence of esterification reaction up to sorbitan monolaurate.

chain-length fatty acid at different temperatures and to determine the optimal temperatures of the reaction of esterification. It is known that sorbitan fatty acid esters can be produced by direct acid (Brown, 1943a,b) and base-catalyzed (Griffin, 1945) reaction of sorbitol with a fatty acid at elevated temperatures. Brown (1943c) describes the preparation of hexide esters either by direct reaction of a hexitol (sorbitol and mannitol) with a fatty acid in the presence of an acid catalyst or by esterification of a hexide by a reaction with an acid halide (e.g., lauroyl chloride) in a medium made basic with pyridine. Soltzberg (1946a) describes the prepara-

tion of monoanhydro sorbitol, which is rich in 1,4-sorbitan, by anhydridation of sorbitol under reduced pressure at 120–150 °C in the presence of an acid catalyst. Soltzberg (1946b) also discloses the preparation of "sorbide" (actually a mixture of isomers) by heating sorbitol solution at reduced pressure (88–95 mmHg absolute) in the presence of an acid catalyst (sulfuric acid) until 2 mol of water/mol of sorbitol are removed. Stockburger (1981) describes the preparation of sorbitan fatty acid esters by forming anhydro sorbitol (a mixture of sorbitans, isosorbide, and unreacted sorbitol) by acid-catalyzed anhydridation, then reacting the



**Figure 5.** Measurement of color by absorbance (at 540 nm) depending on reaction temperatures: (◆) without cyclization; (■) with cyclization.

resulting anhydro sorbitol with a fatty acid in the presence of a base at the temperature not exceeding  $\sim 215$  °C. Use of temperatures not over 215 °C results in products with substantially less color than those obtained at higher temperatures.

The experimental results of this work, specific values of acid concentration at different reaction times at constant temperature, are shown in Figure 2. The relative change of the lauric acid values depended on the reaction time at different temperatures and whether there was (a) no sorbitol cyclization (method A) or (b) the presence of sorbitol cyclization (method B). The conversion of lauric acid was better when sorbitol was previously cyclized (method B).

Two areas of concern when manufacturing sorbitan esters are (1) rate of reaction and the ability to push the reaction to completion and (2) the color of the reaction product. The rate of reaction takes into consideration the kinetic esterification reaction and the catalyst used. The rate of reaction was dependent on the beginning sorbitol anhydrides (1,4-sorbitan and 1,4-3,6-isosorbide).

It is very important to be able to push the reaction to completion. This work was carried out to show the esterification reaction courses at different temperatures. Esterification is an equilibrium reaction, so it was found on the basis of the preliminary esterification experiments without previous sorbitol cyclization (method A) that the esterification reaction is not well approximated by a reversible second-order reaction. During the esterification reaction of sorbitol and fatty acid in the presence of catalysts, reactions of dehydration and cyclization occur simultaneously. The reaction course was changed. Prior to the esterification reaction, sorbitol was cyclized to a mixture of dehydrated products at atmospheric pressure and 140 °C (method B). The obtained results defined the esterification reaction

(method B) as a reversible second-order reaction (Giacometti et al., 1996).

The molar ratio between sorbitol and lauric acid at the beginning of the esterification was 1:1. The amount of fatty acid used is usually in excess of the stoichiometric quantity required for formation of a monoester. The acid catalyst was used because the rate of the esterification reaction (Perka and Ropuszyński, 1972) was faster with an acid catalyst. The catalyst for the sorbitol cyclization and the esterification was *p*-TSA. It is known that increasing temperature results in many secondary reactions and the quantity of sorbitol esters is decreased. However, in this work, it was found out that the *p*-TSA is very specific, because it is possible to course reaction at lower temperature. The esterification reaction can be carried out at 160 °C without decrease of selectivity and product quality. It was proved that the higher part of the catalyst did not impact the quality of the esterification reaction (Grynberg et al., 1970). This catalyst was used because *p*-TSA is not too strong a corrosive reagent for carbohydrate.

The anhydro sorbitol is a mixture of sorbitans (Hopton and Thomas, 1969; 1,4-sorbitan, 2,5-sorbitan, and 3,6-sorbitan), with small amounts of isosorbide and unreacted sorbitol (Perka and Ropuszyński, 1972; Ropuszyński et al., 1969, 1970; Ropuszyński and Sczesna, 1990). 1,4-Sorbitan and 1,4-3,6-isosorbide are the largest constituents of the anhydro sorbitol. The sorbitol cyclization was carried out in 1 h at 140 °C because the unreacted sorbitol was completely converted into a mixture of anhydrides. The reaction of dehydration was finished when all sorbitol was cyclized (Giacometti, 1995) and the esterification began with a mixture of sorbitans.

The reactions of dehydration and esterification were carried out simultaneously in the tests without sorbitol cyclization. The conversion of lauric acid (methods A

and B) at 140 °C is shown in Figure 3. These temperatures were the temperatures of dehydration, and they show a deviation compared with conversions in methods A and B. A better conversion resulted when sorbitol was previously cyclized (method B).

It is advisable to carry out the reactions of dehydration and esterification separately at all examined temperatures. The hypothetical sequence of the esterification reaction up to monolaurate, determined on the basis of the results obtained by the gas chromatography method (Giacometti et al., 1995), is shown in Figure 4.

The color of the reaction product depends on the reaction temperatures and the catalyst used. A dark product of sorbitol esters decreases the possibility of their use. A process that will produce sorbitan esters with more reduced colors than those obtained now, when bleaching agents are not used, is necessary. This problem can be solved by decreasing the reaction temperatures of esterification or by changing the catalyst (Figure 5).

If the color of the reaction product and the rate of reaction are taken into consideration, the optimal temperature was 160 °C. At this temperature, the reaction rate was sufficient, and, in the presence of the catalyst *p*-TSA, formation of undesirable products was avoided.

#### CONCLUSIONS

The conversion of lauric acid was better when sorbitol was previously cyclized (method B). Under controlled conditions, the esterification sorbitol and lauric acid is faster at higher temperatures. The course of esterification of sorbitol and lauric acid can not be followed at temperatures <150 °C. At temperatures >160 °C, with *p*-toluenesulfonic acid as catalyst, the reaction temperature lowers the quality of sorbitan fatty acid esters formed.

#### LITERATURE CITED

- Brown, K. R. U.S. Pat. 2 322 820, 1943a.  
 Brown, K. R. U.S. Pat. 2 322 822, 1943b.  
 Brown, K. R. U.S. Pat. 2 322 821, 1943c.  
 Giacometti, J.; Milin, Č.; Wolf, N. Monitoring the esterification of sorbitol and fatty acids by gas chromatography. *J. Chromatogr. A* **1995**, *704*, 536–540.  
 Giacometti, J.; Wolf, N.; Gomzi, Z.; Milin, Č. Esterification of sorbitol and lauric acid with catalyst *p*-TSA. *React. Kinet. Catal. Lett.* **1996**, in press.  
 Giacometti, J. Department of Chemistry and Biochemistry, Medical Faculty, University of Rijeka. Unpublished results, 1995.  
 Griffin, W. C. U.S. Pat. 2 374 931, 1945.  
 Grynberg, H.; Cyganska, J.; Mazgajska, I. Sorbite dehydration in process of emulsifiers obtaining of fatty acids esters type. *Przem. Chem.* **1970**, *49*, 96–98.  
 Hauthal, H. G. The Third CESIO International Surfactants Exhibition in London 1992. *SÖFW J.* **1992**, *14*, 827–844.  
 Hopton, F. J.; Thomas, G. H. S. Conformations of some dianhydrohexitols. *Can. J. Chem.* **1969**, *47*, 2395–2401.  
 Martinenghi, G. B. Esterificazione. In *Oli, grassi e derivati*, 3rd Ed.; Ulrico Hoepli: Milan, 1963; Chapter 16.  
 Perka, J.; Ropuszyński, S. Examination of the process of esterifying D-sorbitol with higher fatty acids at reduced pressure. *Przem. Chem.* **1972**, *51*, 450–452.  
 Ropuszyński, S.; Matyschok H.; Rzepka, M. Preparation of anhydrosorbites from D-sorbitol at presence of ion-exchanger. *Przem. Chem.* **1969**, *48*, 665–668.  
 Ropuszyński, S.; Jasiński, W.; Perka, J. Preparation of esters of dianhydro-sorbitol and some higher fatty acids. *Przem. Chem.* **1970**, *49*, 222–225.  
 Ropuszyński S.; Sczesna, E. Dehydration of D-sorbitol in the presence of sodium phosphates. *Tenside Surf. Det.* **1990**, *27*, 350–351.  
 Sahasrabudhe, M. R.; Chadha, R. K. Chromatographic analysis of sorbitan fatty acid esters. *J. Am. Oil Chem. Soc.* **1969**, *46*, 8–12.  
 Schuster, G. Einzelbeschreibungen—Herstellung, Zusammensetzung, Eigenschaften. In *Emulgatoren für Lebensmittel*; Springer-Verlag: Berlin, 1985; Chapter C.  
 Soltzberg, S. U.S. Pat. 2 390 395, 1946a.  
 Soltzberg, S. U.S. Pat. 2 387 842, 1946b.  
 Stockburger, G. J. U.S. Pat. 4 297 290, 1981.  
 Turco, A. Emulsioni. In *Nuovissimo ricettario Chimico*; 2nd Ed.; Ulrico Hoepli: Milan, 1980; pp 505–515.

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