

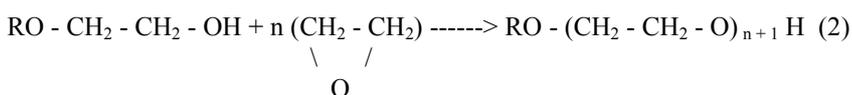
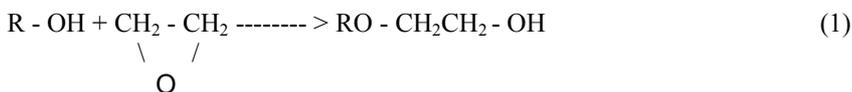
## NONIONIC EMULSIFIERS BASED ON STABILIZED POLIOXIETHYLENE-SORBITANS

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**abstract:** In the present work is studied the synthesis of a nonionic emulsifier and its use for the preparation of emulsified fuels. The nonionic emulsifier is an ester and it was prepared in two ways: the addition of chemical compounds containing active hydrogen (esters obtained out of fatty acids and sorbitol) to an oxyran (ethylene-oxide); the transesterification of the ethoxylated sorbitol with the methylic ester of a fatty acid (oleic acid). The products obtained were further purified through a patented procedure, to obtain stabilized compounds. The ester of oleic acid with sorbitol was obtained by the transesterification of the sorbitol with methyl oleat. The product content of oxietylenic groups was 20-40 relative to a sorbitol molecule. The synthesized emulsifiers were tested for the preparation of emulsified oil-in-water fuels used for burning processes improvement and implicitly reductions of pollutants.

### Introduction

The polycondensation of a compound containing hydroxilic groups (alcohol, poliol, alkylphenol, carboxylic acid) with ethylene oxide can be schematically represented through the following chemical reactions:



The polycondensation reactions can occur non-catalytically, at a high temperature and pressure, or catalytically, in the presence of alkaline hydroxids or strong acids, at moderate temperatures and pressures. The usage of acid catalysts is limited by the production of polyalkylglycols which have small molecular weights and a very large distribution of the molecular weights.

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One of the domains in which the transesterification with a single development is applied is the synthesis of the esters obtained out of fatty acids and polyhydric compounds. Thus, the polyhydric compounds such as glycerine, diglycerine, polyglycerine, xylitol, sorbitol, mannitol, saccharose and other polyglycoside, lead, by the partial esterification with fatty acids, to products presenting tensioactive properties. The hydrophilicity of these esters can be enhanced through the ethoxylation of the unesterified hydroxilic groups.

The sorbitol esters are very important due to fact that sorbitol is easily available (it is obtained by the simple reduction of glucose) and also due to the fact that sorbitol has a relatively higher thermic stability than saccharose. Sorbitol can be converted into monoesters or polyesters through the reaction with acid chlorides of the fatty acids in mild conditions, in the presence of pyridine. In industry, the esterification is produced using fatty acids or their methylic esters.[1] Along with the sorbitol which does not react, the reaction product contains monoesters or diesters obtained of fatty acids and sorbitol. Triesters are only formed in small percents.

A process for the synthesis of nonionic tensioactives was implemented using as raw material the saccharose instead of the sorbitol.[2] The ethoxylation at 120<sup>0</sup>C took place in a first stage, followed by the transesterification of the fatty acid esters at 100<sup>0</sup>C in the presence of a catalyst like potassium bicarbonate or at 180<sup>0</sup>C in the presence of a catalyst like hydrochloric acid. Optionally a solvent can also be used and the transesterification can take place in the presence of an enzyme.[3]

In the majority of cases, emulsions are prepared with the aid of one or more emulsifiers, usually with different HLB values. The emulsifier is either dissolved or pre-emulsified in the oil or water phase, and this solution is then worked into the external phase, or the external phase is slowly added to the emulsifier-oil mixture. Whether an ionic or nonionic emulsifier is used for emulsifying depends on the system. Nonionic emulsifiers are also often used to prepare o/w emulsions.

The usage of nonionic emulsifiers for the preparation of emulsions based on oil-based products is recent. Thus, in a recent paper [4] it has been studied the behaviour of 13 nonionic surfactants for the preparation of bituminous o/w emulsions. It has been noticed that the emulsifiers used to prepare oil in water (o/w) emulsions are soluble in the aqueous phase and they have an HLB ranging from 9,6 to 17,6 and that the emulsifiers used to prepare water in oil (w/o) emulsions have an HLB ranging from 4,7 to 6,7, being soluble in the oily phase.

A different paper [5] describes a composition and a method for obtaining a w/o emulsion. This invention is related to a composition of the emulsifier forming a w/o emulsion with an exceptional stability as far as stocking is concerned. The emulsifier is a mixture made of dibehenilfumarate, the distearic ester of PEG 1500 and the stearic acid's monoethanolamine. The emulsifier thus prepared even manages to stabilize emulsions with a high content of water (50-90%).

The hydrophobic/hydrophilic properties of the emulsions prepared with such emulsifiers can be controlled by the selection of the fatty acid type, by the degree of ethoxylation and through cosurfactants addition respectwely.

## Experimental

The reaction of ethoxylation was conducted in liquid phase, in a stirred reactor equipped with a heating coil using isothermic and isobaric conditions. The stirrer is acted by means of magnetic coupling. The heating agent is supplied by a thermostat, the temperature in the reactor being measured with a thermocouple and the pressure with a manometer. The stirring speed is adjusted using a potentiometer. The supply of oxiran is taken from a gas cylinder coupled with a calibrated vessel equipped with level-indicating glass.

The reactor's inertisation as well as the oxiran dosage is made using nitrogen. The successive operations of voiding – inertisation of the reactor in order to eliminate the air, are performed with an air pump.

The reaction took place under a nitrogen layer between 110-130<sup>0</sup>C temperatures. The process of ethoxylation is performed semicontinuously, the compound which is to be ethoxylated being introduced in the first stage, and then the ethylene oxide being gradually added with controlled rate, using in this aim the calibrated vessel with level-indicating glass. The catalyst used, the potassium hydroxide, is added as an aqueous solution, by dosing it in small amounts, before the feed of the ethylene oxide.

The reaction product was purified in a laboratory column-like reactor, with a view to retaining the alkaline metallic ions on the strong acid, cation-exchanger resin (PUROLITE CT 175).

The process of transesterification was performed in a three-necked glass flask under continuous mechanical mixing. The heating was provided with the help of an electric calotte equipped with a potentiometer for the adjustment of the heating rate.

The reaction of the sorbitol with the fatty acid esters was performed at 110-130<sup>0</sup>C temperature, in the presence of an alkaline catalyst at atmospheric pressure or under a slight vacuum. The catalyst used was the potassium hydroxide with a concentration of max. 1% relative to the sorbitol, dissolved in methanol.

The experimental program performed with the purpose of determining the emulsifying characteristics of nonionic, sorbitol-based emulsifiers, took place on a micropilot, colloidal mill of the EMULBITUME type.

The raw materials used for the synthesis of the etoxilated products were: the ethylene oxide, the sorbitol and the methyl-oleate of analytical purity.

## Results and discussions

The plot of Fig. 1 represents the specific ethylene oxide consumption in time during sorbitol ethoxylation at 110<sup>0</sup>C and 4 atm.

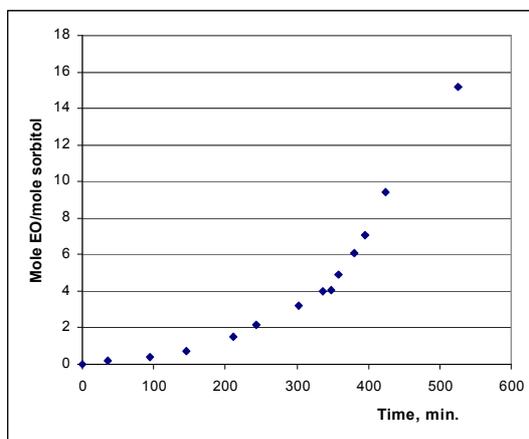


Fig. 1. Specific ethylene oxide (EO) consumption in time during sorbitol ethoxylation

( $t = 110\text{ }^{\circ}\text{C}$ ,  $p = 4\text{ atm}$ ,  $\text{KOH}:\text{Sorbitol} = 0.6:100$ )

As one can see from Figure 1, the reaction present an induction period when the process follow with low rate, behaviour probable due to relative high acidity of sorbitol. The influence of the catalyst's concentration on the reaction of sorbitol ethoxylation was emphasized in Figure 2, and the influence of the pressure on the ethoxylation process was evidenced Figure 3.

In Figure 4 is graphically represented the variation of the specific ethylene oxide consumption in respect with time, for the ethoxylation of sorbitan di-oleate, comparing it to the ethoxylation of sorbitol, in the same working conditions.

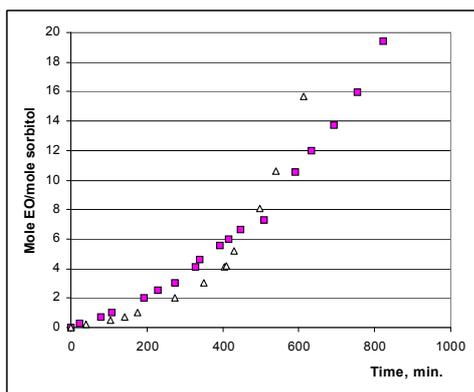


Fig. 2. Effect of catalyst concentration on specific consumption of EO (sorbitol ethoxylation)

( $t = 100\text{ }^{\circ}\text{C}$ ,  $p = 4\text{ atm}$ ,

( $\square$ )  $\text{KOH}:\text{Sorbitol} = 0.2:100$ , ( $\Delta$ )  $\text{KOH}:\text{Sorbitol} = 0.4:100$ )

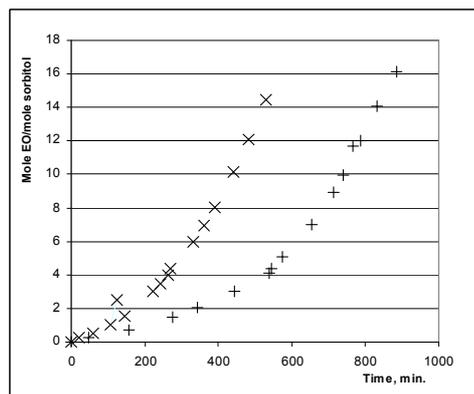
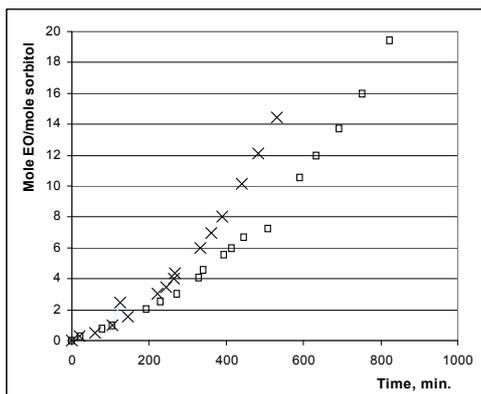


Fig. 3. Pressure effect on specific consumption of EO (sorbitol ethoxylation)

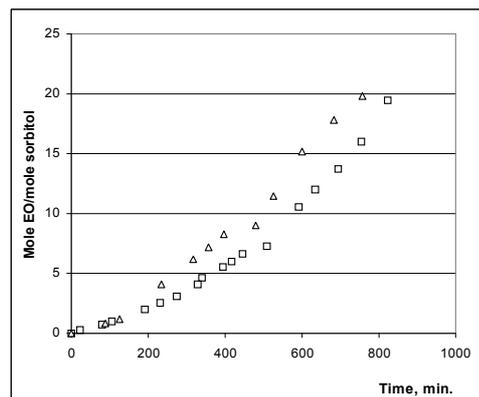
( $t = 110\text{ }^{\circ}\text{C}$ ,  $\text{KOH}:\text{Sorbitol} = 0.2:100$ ,

( $+$ )  $p = 3\text{ atm}$ , ( $\times$ )  $p = 4\text{ atm}$ )

In Figure 5 we comparatively present the ethoxylation of sorbitol for two different temperatures (100°C and 110°C).



**Fig. 4.** Temperature effect on specific consumption of EO (sorbitol ethoxylation)  
( $p = 4 \text{ atm}$ ,  $\text{KOH}:\text{Sorbitol} = 0.2:100$ ,  
(□)  $t = 100^\circ\text{C}$ , (+)  $t = 110^\circ\text{C}$ )



**Fig. 5.** Time variation of specific EO consumption for different substrates  
(□) sorbitol, (Δ) sorbitan dioleate

The experimental program of transesterification included 6 experience (see table1) using sorbitol or sorbitol ethoxylated with 20 molecules of ethylenoxide. The reaction temperature varied between 120-210°C. The analysis of reaction progress was performed by measuring the saponification value.

The experimental observations evidenced the fact that the rise of the temperature over 135°C favors the dehydration-condensation reactions conducting to caramel type by-products, this diminishing the selectivity in ester.

The tendency of the sorbitol condensation to caramel through shutting off the hydroxilic groups decrease if the ethoxilation stage is realized before the transesterification stage.

**Table 1. Transesterification of sorbitol and ethoxylated sorbitol with methyl oleate**

Nr crt	Sort of sorbitol	Temp. [°C]	Pressure	Catalyst concentration [%]	$R_m^*$ E / S	Time of reaction [h]	Saponification value [mgKOH/g]
	Not-ethoxylated						
1.	Not-ethoxylated	130	vacuum	0,8	4	16	244,2
2.	Not-ethoxylated	120	vacuum	0,8	3	16	189,9
3.	Not-ethoxylated	135	vacuum	0,8	2	16	179,9
4.	Not-ethoxylated	120	vacuum	0,8	2	16	68,7
5.	Etoxylat	210	atmospheric	0,4	2	8	63,9
6.	Etoxylat	170	atmospheric	0,4	2	8	62,4

$R_m^*$  E / S –Molar ratio between sorbitol and ester

This emulsifiers were tested in the preparation of fuels emulsions in the following conditions:

- temperature of the organic phase : 80<sup>0</sup>C
- temperature of aqueous phase : 40<sup>0</sup>C
- content of the emulsifier : 1%
- weight ratio between organic phase and aqueous phase: 3/1
- rotation speed of atomix: 6000 rpm

The main characteristics of fuel emulsions obtained are :

- type of the emulsions: oil in water
- viscosity at 25<sup>0</sup>C: 3,6-3,8<sup>0</sup>E;
- stability: emulsion stable at 30 days after preparation.

## Conclusions

The conclusions of this work can be drawn in the following points:

- the ethoxylation process of sorbitol present an induction period when the reaction follow with low speed, behaviour probable due to relative high acidity of sorbitol; after formation of the monoethoxylat intermediary product, the raw material acidity lowed and the process speed is stabilized at higher values.
- the increase of the catalyst's concentration increase the reaction rate without significant influence of the process rate in the induction period.
- the workin pressure influence in an important measure the reaction rate due to increase of the ethylenoxide concentration in liquid phase.
- the sorbitan di-oleate is ethoxylated with the higher rate than sorbitol in the same reaction conditions; the induction period is shorter than in the sorbitan di-oleate ethoxylation.
- the thermal stability of sorbitol is lower at temperature higher than 120<sup>0</sup>C.
- the yield of the transesterification process is favorized by performing the process in vacuum.
- the fuels emulsions stability obtained with derivatives of ethoxylated oleic acid have the same stability as the cationic emulsions.

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