Journal of Chemical Technology and Metallurgy, 56, 2, 2021, 268-274

OPTIMIZATION OF ULTRASOUND SYNTHESIS OF SUCROSE ESTERS BY SELECTION OF A SUITABLE CATALYST AND REACTION CONDITIONS

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Received 25 October 2019
Accepted 10 January 2020

ABSTRACT

Sucrose is used as a renewable raw material for the preparation of esters in various fields such as detergents, whitening boosters, cosmetics, medicines, nutritional supplements, emulsifiers, stabilizing agents, etc. By transesterification of all hydroxyl groups with fatty acids, the polysubstituted sucrose esters acquire specific physical and organoleptic properties of fats. Sucrose esters, with three or less substituted OH groups with fatty acids, are suitable as surfactants and nutritional supplements due to their emulsification, stabilizing and conditioning properties.

The main problem with the synthesis of sucrose esters relates to the high functionality of the sucrose molecule - eight hydroxyl groups that compete during the synthesis and lead to the formation of mixtures of monoesters, diesters and even higher esters. Transesterification can be oriented to a specific substitution model by carefully selecting the reaction conditions. Therefore, the focus of this study was to clarify the effects of the sucrose to fatty acid molar ratio, catalyst and reaction temperature on the rate of sucrose ester formation in a specific substitution mode (monoesters).

Keywords: sucrose, transesterification, ultrasound synthesis, sucrose esters.

INTRODUCTION

The interest in sucrose esters, which are surfactants and environmental products by themselves, has attracted the attention of researchers and manufacturers due to the fact that renewable, readily available and inexpensive raw materials, such as sucrose and fats/oils, are used to prepare them. Sucrose esters are non-toxic, biocompatible and biodegradable products [1], which are widely used in food technology, cosmetics and medicine. The industrial synthesis of esters is based on the chemical esterification of fatty acids with alcohol in the presence of inorganic catalysts at high temperatures. These chemical processes are equivalent and are therefore slow, non-selective, consuming large amounts of energy and have low productivity. A number of industrial technologies generate waste that creates the risk of environmental pollution. In this regard, research in recent years has focused on the search for new technological solutions to intensify the processes. For solution reactions, the use of ultrasound is effective. Ultrasound has been found to influence the rate of chemical reactions in solution through the phenomenon of cavitation and the generation of microbubbles. This process can be characterized by the formation, growth and implosive disintegration of gas bubbles in the solution. During their decomposition, as a result of the cavitation, extremely high pressure and temperature are generated inside the microbubble. This unique energy is a means of interaction of substances in solution.

The use of principles of "green" chemistry like ultrasound and microwave energy in modern technologies is widespread - in organic synthesis and modification of organic compounds, for the degradation of environmental pollutants, in medicine, etc. [2 - 13].

A research into the use of ultrasound in the synthesis of esters is promising in organic synthesis. The defined goals comprise a reduction of the reaction time, an increase of the yield, a use of safe raw materials and a decrease of energy consumption. Its effect on the esterification process in the preparation of aliphatic and sucrose esters of short-chain and medium-chain fatty acids has not yet been sufficiently studied.

EXPERIMENTAL

Reagents

Lauric acid, 10-undecylenic acid (Alfa Aesar), palmitic acid (Reachim), anhydrous Na_2SO_4 (Riedel-de-Hauln), concentrated sulfuric acid, K_2CO_3, NaCl, n -butanol, sucrose, NaH_2PO_4 (Chimtex), diethyl ether (Panreac), CH_3ONa were obtained by the method described by Fizer& Fizer [14].

Methods for esters synthesis

Conventional synthesis. Methanol (50 cm^3) and 0.018 mol of methyl ester of the corresponding fatty acid, sucrose and K_2CO_3 catalyst (0.1 mol) were placed in an Erlenmeyer flask of 100 cm^3. The flask was placed in a water bath at 40°C and 65°C. The reaction temperature was controlled by using a thermostat. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction (duration 120 min), the solvent was distilled under vacuum. The residue was dissolved in 25 % NaCl / n-butanol (1:1, v/v) and the mixture was separated by a separation funnel. A threefold extraction with 20 cm^3 n-butanol was performed. The combined extracts were dried with anhydrous Na_2SO_4 and the solvent was distilled under vacuum.

Ultrasonic synthesis. 50 cm^3 of methanol and 0.018 mol of methyl ester of the corresponding fatty acid, sucrose and catalyst (0.1 mol) were placed in an Erlenmeyer flask of 100 cm^3. The flask was connected to a water-cooled reflux condenser and processed it in Dimoff A-2/2 (100 W, 44 kHz) ultrasonic bath at 40°C and 65°C. The reaction temperature was controlled by using a thermostat. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction (after 60 min) the solvent was distilled at vacuum. The residue was dissolved in 25 % NaCl/n -butanol 1:1 (v/v) and the mixture was separated by a separation funnel. A threefold extraction with 20 cm^3 n-butanol was performed. The combined extracts were dried with anhydrous Na_2SO_4 and the solvent was distilled in vacuo.

Identification of the esters obtained. Fourier transform infrared spectroscopy (FT-IR) was used to identify and characterize the esters obtained. The spectra were recorded on a Nicolet Avatar spectrometer (Termo Scientific, USA) in a KBr tablet, in the range of 4000 cm^{-1} - 400 cm^{-1}. The NMR spectra (^{1}H and ^{13}C) of the synthesized esters were recorded on a Bruker spectrometer (500 MHz) in $CDCl_3$ solution and a standard tetramethylsilane.

RESULTS AND DISCUSSION

Characterization of the obtained sucrose esters

FT-IR Spectroscopy

All samples for FT-IR spectra were pressed into KBr tablets. The spectra contained several bands in some regions specific to carbohydrates. In the first of them, about 3300 cm^{-1}, there is a wide asymmetric band due to the stretching vibrations of the –OH group. The strong interaction between the functional groups of the macromolecules in the modified sucrose is the reason in the spectrum considered, bands arise due to complex vibrations, which can be defined as oscillations of both the furanose ring and the macromolecule as a whole. The stretching vibrations (C–C), (C–O), (C–O–C) of the furanose structure are observed between 1000 cm^{-1} and 1200 cm^{-1}.

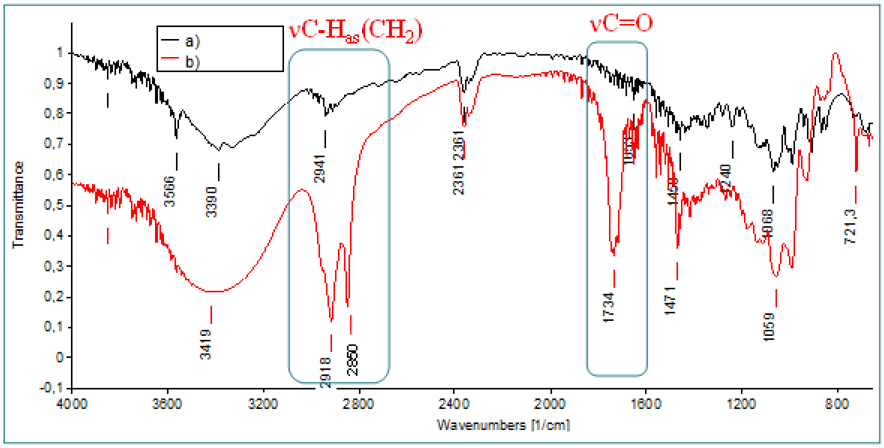

Fig. 1. IR spectrum of: a) sucrose; b) synthesized sucrose palmitate.

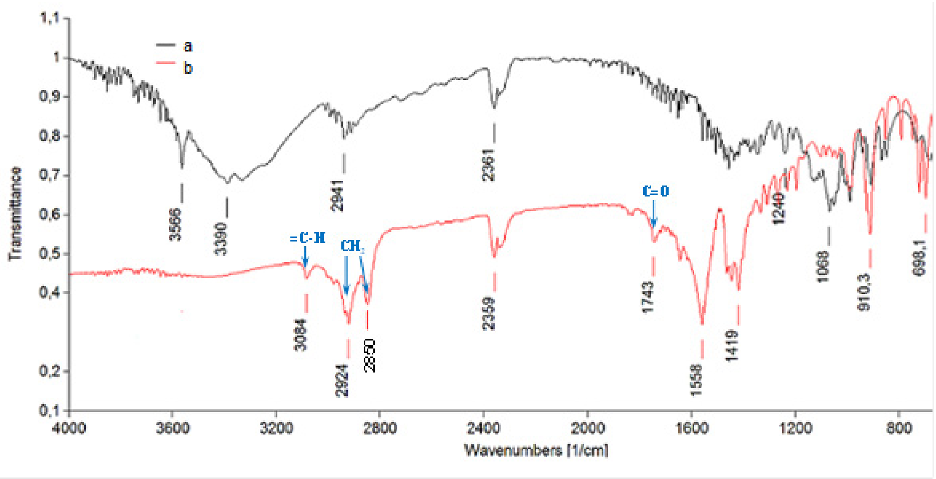

Fig. 2. IR spectrum of sucrose (a) and synthesized sucro-10-undecylenate (b).

Depending on the degree of substitution, the maximum of this band is shifted and at the same time the half-width changes. This is due to the hydroxyl groups which form the hydrogen bonds as well as to the esterification of some of them.

A new band in the spectrum of the sucrose palmitate (Fig. 1) is clearly visible in the spectrum of esters at 1734 cm^{-1} due to the stretching vibrations ($\nu_{C=O}$) of the ester. The presence of such a band at 1720 cm^{-1} - 1728 cm^{-1} was reported by Song [15] in sucrose octanoates (ester obtained by transesterification of sucrose with ethylcaprylate), as well as in the spectrum of sucrose octanoate obtained by ultrasonic synthesis [16].

Fig. 2 represents the FT-IR spectrum of sucro-10-undecylenate synthesized at ultrasound. The IR spectrum of sucro-10-undecylenate contains the characteristic features of the strips of synthesized sucrose esters described so far - reducing the intensity to 3300 cm^{-1} with the appearance of a band at about 1743 cm^{-1} typical of ν(C=O), but others appear, too.

The detection of bands at 3083 cm^{-1} ν(C=O) and 1652 cm^{-1} ν(C=C) demonstrated the presence of a double bond of the vinyl group, which confirms the attachment of 10-undecylenic residue to sucrose, as well as maintaining the stability of the ester during the synthesis.

NMR spectroscopy

In the ^{1}H NMR spectrum of sucrose esters, in particular sucrose palmitate, two regions can be distinguished - in the range 0 - 3.0 ppm, which is typical for methyl and methylene protons from acid and 3.0 - 6.0 ppm, which is typical for protons of the carbohydrate moiety, are shown in Table 1. Chemical displacements for protons of methyl groups in sucrose palmitate and

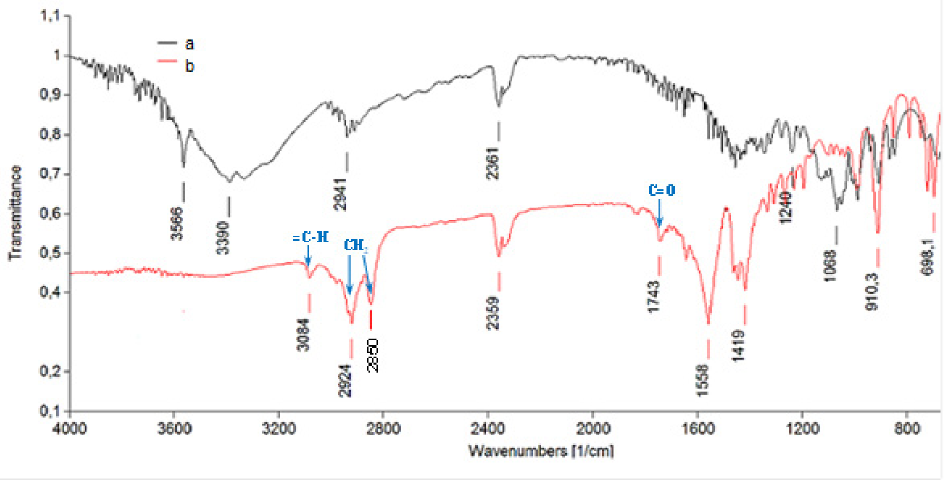

Fig. 2. IR spectrum of sucrose (a) and synthesized sucro-10-undecylenate (b).

Table 1. Chemical displacement (δ, ppm) in the ^{1}H NMR spectrum of the synthesized sucrose esters.

Group	Sucrose-palmitate	Sucrose-caprinate	Sucrose-10-undecylenate
C**H**$_3$–	0,87~0,89	0,96~0,99	–
C**H**$_2$=	–	–	4,95~5,01
–C**H**=	–	–	5,61~5,69
–(C**H**$_2$)$_n$–	1,17~1,37	1,31~1,68	1,69~2,02
–(CH$_2$)$_n$–C**H**$_2$–O	2,27~2,35	2,34~2,36	2,31~2,34
–O–C**H**–O	5,43	5,39~5,40	5,40
H-Glc	3,39~5,38	3,39~5,40	3,34~5,40
H-Fru	3,58~4,39	3,62~4,52	3,50~4,50

sucrose caprine were observed at 0.87 ~ 0.99 ppm.

The proton signals from the methylene groups and the four synthesized esters were in the range of 1.17 ~ 2.02 ppm. The two vinyl protons of the mono-substituted group in the sucro-10-undecylenes were observed at 4.95 ~ 5.01 ppm (=CH_2) and the single one at 5.61 ~ 5.69 ppm (–CH=). Glucose protons of glucopyranose are observed in the range of 3.34 ~ 5.40 ppm, and glucose protons of fructofuranose at 3.50 ~ 4.50 ppm.

In ^{13}C NMR spectra of the synthesized sucrose esters (Table 2) typical signals of carbonyl carbon were observed at 174.36 ppm - 175.12 ppm (for sucrose palmitate, caprinate and 10-undecylenate). The signals for carbon atoms from the monosubstituted double bond in sucro-10-undecylenes are observed at 115.35 ppm (for H_2C =) and at 139.00 ppm (for -CH=).

The signals from methyl carbon atoms were observed in the range of 14.12 ppm - 20.65 ppm. The signals of the carbon atoms of the pyranose, respectively, of the furanose ring, were observed in the range 61.18 ppm - 108.18 ppm, with carbon atoms of the pyranose ring being at the lower frequencies and for the furanose at the higher frequency range.

Optimization of factors affecting the synthesis of sucrose esters

In order to optimize the conditions of the transesterification reaction on the yield of sucrose esters, the influence of the following parameters on the reaction time and product yield was investigated:

molar ratio of ester: sucrose - 1:1 and 3:1;

catalyst type - CH_3ONa, K_2CO_3, NaH_2PO_4;

catalyst molar ratio - 0.1; 0.3; 0.5.

The effect of the molar ratio and the type of catalyst used on the yield and reaction time at an ester: sucrose mole ratio of 1:1 and 3:1 with solvent CH_3OH is presented in Table 3.

On the basis of the comparative analysis of the data on the catalysts used in conventional and ultrasonic synthesis, it can be concluded that K_2CO_3 and CH_3ONa are more suitable as catalysts. The use of sodium dihydrogen phosphate does not lead to a significant increase in the yield.

The salts of a more basic nature are better catalysts for transesterification, which has a logical connection

Table 2. Chemical displacement (δ, ppm) in the ^{13}C NMR spectrum of the synthesized sucrose esters.

Group	Sucrose-palmitate	Sucrose-caprinate	Sucrose-10-undecylenate
C**H**$_3$–	0,87~0,89	0,96~0,99	–
C**H**$_2$=	–	–	4,95~5,01
–C**H**=	–	–	5,61~5,69
–(C**H**$_2$)$_n$–	1,17~1,37	1,31~1,68	1,69~2,02
–(CH$_2$)$_n$–C**H**$_2$–O	2,27~2,35	2,34~2,36	2,31~2,34
–O–C**H**–O	5,43	5,39~5,40	5,40
H-Glc	3,39~5,38	3,39~5,40	3,34~5,40
H-Fru	3,58~4,39	3,62~4,52	3,50~4,50

Table 3. Effect of molar ratio of ester:sucrose and type of catalyst on the reaction time and the yield of sucrose palmitate.

Catalyst	Molar ratio of catalyst	Ester	*molar ratio of ester: sucrose 1:1*		*molar ratio of ester: sucrose 3:1*	
			yield, %		yield, %	
			Conventional method	US	Conventional method	US
K_2CO_3	0,1	Sucrose palmitate	65±0.3	80±0.2	67±0.3	81±0.4
		Sucrose caprinate	68±0.2	82±0.2	66±0.3	80±0.3
		Sucrose-10-undecylenate	65±0.2	80±0.2	68±0.3	82±0.4
	0,3	Sucrose palmitate	68±0.3	83±0.3	70±0.2	83±0.3
		Sucrose caprinate	68±0.3	83±0.2	71±0.2	82±0.3
		Sucrose-10-undecylenate	65±0.2	82±0.3	70±0.2	83±0.4
	0,5	Sucrose palmitate	70±0.3	85±0.2	72±0.4	85±0.3
		Sucrose caprinate	69±0.2	83±0.3	74±0.4	85±0.4
		Sucrose-10-undecylenate	71±0.3	81±0.2	70±0.4	84±0.2
CH_3ONa	0,1	Sucrose palmitate	70±0.2	87±0.2	75±0.3	87±0.2
		Sucrose caprinate	71±0.3	85±0.3	75±0.2	88±0.3
		Sucrose-10-undecylenate	72±0.4	83±0.3	73±0.4	85±0.2
	0,3	Sucrose palmitate	75±0.3	87±0.2	78±0.3	88±0.3
		Sucrose caprinate	74±0.2	86±0.3	77±0.3	85±0.3
		Sucrose-10-undecylenate	74±0.3	88±0.2	78±0.3	84±0.3
	0,5	Sucrose palmitate	85±0.2	90±0.3	87±0.2	92±0.2
		Sucrose caprinate	84±0.3	93±0.2	85±0.3	90±0.3
		Sucrose-10-undecylenate	85±0.2	92±0.3	85±0.4	92±0.2
NaH_2PO_4	0,1	Sucrose palmitate	0±0.3	4±0.2	0±0.3	4±0.2
		Sucrose caprinate	0±0.2	2±0.2	0±0.3	3±0.2
		Sucrose-10-undecylenate	1±0.2	2±0.3	0±0.3	3±0.2
	0,3	Sucrose palmitate	2±0.3	5±0.3	3±0.3	5±0.2
		Sucrose caprinate	3±0.2	4±0.3	2±0.3	4±0.2
		Sucrose-10-undecylenate	4±0.3	4±0.4	3±0.3	4±0.2
	0,5	Sucrose palmitate	5±0.2	7±0.2	6±0.3	7±0.2
		Sucrose caprinate	4±0.3	6±0.3	4±0.3	6±0.2
		Sucrose-10-undecylenate	5±0.2	6±0.3	5±0.3	6±0.2

with the reaction mechanism. Although CH_3ONa is more expensive and its preparation is more specific, it is recommended to use it for better efficiency.

Under the chosen reaction conditions, the change in the catalyst molar ratio results in a slight increase in the yield. For this reason, experiments were performed with a catalyst to sucrose molar ratio of 1:1. A threefold increase in the amount of ester results in a slight increase in yield, which indicates that the amount of sucrose limits the reaction time.

The effect of temperature, the molar ratio of ester: sucrose and the type of catalyst (0.1 mol) on sucrose palmitate yield are presented in Table 4.

The yield of sucrose palmitate obtained was highest using sodium methylate catalyst (85 % - 95 %), a lower yield was observed using K_2CO_3 (76 % - 80 %), while using NaH_2PO_4 did not produce a significant resulting yield.

The reaction temperature when using the US effect has both a positive effect - it increases the yield (up to 10 %) and a negative one - it reduces the field efficiency.

Table 4. Effect of temperature and catalyst type (0.1 mol) on sucrose palmitate yield at ester: sucrose molar ratio of 1:1 and 3:1.

T, °C	molar ratio of ester:sucrose	Catalyst	Ester	yield, %
40	3:1	CH_3ONa	Sucrose palmitate	87±0.2
40	3:1	CH_3ONa	Sucrose caprinate	88±0.2
40	3:1	CH_3ONa	Sucrose-10-undecylenate	85±0.2
40	3:1	NaH_2PO_4	Sucrose palmitate	4±0.2
40	3:1	NaH_2PO_4	Sucrose caprinate	3±0.2
40	3:1	NaH_2PO_4	Sucrose-10-undecylenate	3±0.2
40	3:1	K_2CO_3	Sucrose palmitate	81±0.2
40	3:1	K_2CO_3	Sucrose caprinate	80±0.2
40	3:1	K_2CO_3	Sucrose-10-undecylenate	82±0.2
40	1:1	CH_3ONa	Sucrose palmitate	87±0.2
40	1:1	CH_3ONa	Sucrose caprinate	85±0.2
40	1:1	CH_3ONa	Sucrose-10-undecylenate	83±0.2
40	1:1	NaH_2PO_4	Sucrose palmitate	4±0.2
40	1:1	NaH_2PO_4	Sucrose caprinate	2±0.2
40	1:1	NaH_2PO_4	Sucrose-10-undecylenate	2±0.2
40	1:1	K_2CO_3	Sucrose palmitate	80±0.2
40	1:1	K_2CO_3	Sucrose caprinate	82±0.2
40	1:1	K_2CO_3	Sucrose-10-undecylenate	80±0.2
65	3:1	CH_3ONa	Sucrose palmitate	95±0.2
65	3:1	CH_3ONa	Sucrose caprinate	93±0.2
65	3:1	CH_3ONa	Sucrose-10-undecylenate	94±0.2
65	3:1	NaH_2PO_4	Sucrose palmitate	5±0.2
65	3:1	NaH_2PO_4	Sucrose caprinate	4±0.2
65	3:1	NaH_2PO_4	Sucrose-10-undecylenate	5±0.2
65	3:1	K_2CO_3	Sucrose palmitate	83±0.2
65	3:1	K_2CO_3	Sucrose caprinate	85±0.2
65	3:1	K_2CO_3	Sucrose-10-undecylenate	82±0.2
65	1:1	CH_3ONa	Sucrose palmitate	85±0.2
65	1:1	CH_3ONa	Sucrose caprinate	83±0.2
65	1:1	CH_3ONa	Sucrose-10-undecylenate	85±0.2
65	1:1	NaH_2PO_4	Sucrose palmitate	3±0.2
65	1:1	NaH_2PO_4	Sucrose caprinate	4±0.2
65	1:1	NaH_2PO_4	Sucrose-10-undecylenate	2±0.2
65	1:1	K_2CO_3	Sucrose palmitate	76±0.2
65	1:1	K_2CO_3	Sucrose caprinate	75±0.2
65	1:1	K_2CO_3	Sucrose-10-undecylenate	75±0.2

Therefore, the results do not show a significant advantage in using a higher reaction temperature.

CONCLUSIONS

The significant intensifying effect of the ultrasonic irradiation on the production of sucrose esters from saturated higher fatty acids - capric, palmitic and unsaturated higher fatty acid - 10-undecylenic, has been demonstrated.

As a result, the reaction time was reduced and the reaction temperature was lowered. Under the conditions of ultrasonic synthesis studied, the composition of the esters obtained was the same as that obtained by the conventional method. By means of spectral methods (FT-IR and NMR-spectroscopy), it was unambiguously established that under the chosen synthesis conditions, any carbon-carbon bond breakage, isomerization and auto-oxidation of the reaction products were not observed. Therefore, the application of ultrasonic irradiation for synthesis of sucrose esters presented the better approach comprising the advantages as reducing time and increasing yields.

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