� Organic Reactions in Emulsions — Preparation of Glycerol and Polyglycerol Esters of Fatty Acids by Transesterification Reaction

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ABSTRACT

Monoglycerol and polyglycerol esters of fatty acids have been prepared in an emulsion medium of polyglycerol in esters of fatty acids. Transesterification between glycerol or polyglycerols and methyl esters of fatty acids is made at relatively low temperatures (95-150 C) in the presence of alkaline catalyst and anionic or nonionic emulsifiers. The reaction system consists of two immiscible phases transformed into a "milky" (macro) or transparent (micro) emulsion throughout the heating process. The product obtained using this technology is not a highly substituted ester since the transesterification reaction is selective. The type and the amount of emulsifier have to be carefully selected. Unsuitable emulsifiers which will not stabilize the emulsion are ineffective in enlarging the contact between the reactants; therefore, the conversion of the reactants is very poor. With suitable emulsifiers, the conversions and the yields improved due to a better contact between reactants.

INTRODUCTION

Glycerol and polyglycerol esters of fatty acids are industrially prepared and commercially available as food, cosmetic and pharmaceutical emulsifiers (1,2). The main industrial process (3) is based on direct esterification of fatty acids with polyglycerols of various chain lengths in the presence of alkaline catalyst at elevated temperatures (200-250 C). The reaction is tedious, nonselective, energy-consuming and the crude product usually needs further filtration, purification and bleaching processes (3).

Many of the available polyglycerol esters consist of various polyglycerol chain lengths, fatty acids and degrees of esterifications. The final product will have the required hydrophile-lipophile balance, (HLB) according to the ratio of the reactants and reaction conditions. However, the control of the number of substitutions on the polyglycerol chain and the isomers obtained cannot be easily regulated (4) and, as a result, the activity of the emulsifier is not well controlled or defined.

The microemulsion process for the preparation of sucrose esters was first suggested by Osipow and Rosenblatt (5) and has been applied commercially. Osipow and Rosenblatt also mentioned the possibility of preparing monoglycerol esters of fatty acids by this method, but the microemulsion method has not yet been extensively studied or applied.

This paper is an evaluation and an extensive study of Osipow and Rosenblatt's conception for the transesterification reaction between glycerol or polyglycerols and methyl esters of fatty acids with or without cosolvents, such as propylene glycol, in the presence of alkaline catalyst and nonionic or ionic emulsifiers. The formation of glycerol or polyglycerol in oil emulsions has been suggested. The final product is relatively pure and has improved color due to the low temperatures applied in the process. We use glycerol or polyglycerols both as reaction media and reactants. An emulsion is formed, and transesterification reaction is carried out between the methyl esters of fatty acids and glycerol or polyglycerol.

EXPERIMENTAL

Materials

Commercially available methyl stearate (95% methyl stearate and 5% methyl palmitate) and methyl myristate (99%) were purchased from Aldrich Chemical Company Inc. Sodium stearate was obtained from Riedel-De Haenag; Ca-stearate from Hopkin and Williams, Ltd.; and Mg-stearate was prepared in our laboratories. Cetyltrimethylammoniumbromide (CMAB) was from Fluka AG; sorbitan monooleate (Span 80), sorbitan monostearate (Span 60), sorbitan monopalmitate (Span 40), sorbitan monolaurate (Span 80); ethoxylated sorbitan monooleate (Tween 80); ethoxylated sorbitan monostearate (Tween 60) and polyoxyethylene stearyl ether (Brij 72) were from Atlas Europol A.s.P. Triglycerol monooleate (3G10) was obtained from Capitol City Products; monodiglyceride (MDG) was from Hercules Inc.; and Na_2CO_3, K_2CO_3, $MgCO_3$ and $CaCO_3$ were from BDH Chemicals Ltd. Polyglycerols were prepared in our laboratories (3) from 98% BDH glycerol.

Procedure

A typical transesterification reaction was done by adding the appropriate amount of glycerol or tetraglycerol to the molten methyl stearate. Catalytic amounts of NaOH (0.15% of the reactants) together with ionic or nonionic emulsifiers (0-15 wt % of the oil phase) were charged into the reaction vessel while stirring and heating the system to 95-150 C. Samples were withdrawn for gas liquid chromatographic (GLC) and high pressure liquid chromatographic (HPLC) analyses and for determination of glycerol and polyglycerol monoester content. There was no need for applying vacuum or inert gas stream.

Analysis

The amount of methyl stearate consumed during the reaction was determined by GLC using a 3 ft x 1/8 in. 3% OV-17 glass column at 185 C; methyl myristate (99%) was used as an external standard. Glycerol and polyglycerol monostearate contents were determined using the periodic acid method (6).

For HPLC, a Model SP 8000 (Spectra Physics) equipped with a UV SP-770 variable wavelength detector (Schoeffel Instruments Corp.) at 220 nm, and 250 x 4.6 mm stainless steel 10-μ Lichrosorb-Diol column, was used to determine the formation of glycerol mono-, di- and tristearate and of tetraglycerol mono-, di- and tristearate. The eluent was hexane/isopropanol (HPLC grade, Bio-Lab LTD. Laboratories) used in a gradient manner (7).

RESULTS

The first aim of this study was to prove the formation of an

emulsion and the necessity of both the catalyst and the emulsifier for high reaction yields.

In several preliminary reactions, equimolar amounts of glycerol were added to a molten methyl stearate and stirred vigorously at 130 C for several hours. An immediate separation of the two phases occurred upon turning off the stirring. The glycerol settled to the bottom of the reaction flask and the unreacted methyl stearate was found floating to the top. No transesterification occurred even after 24 hr of mixing.

In a test reaction, it was shown that sodium hydroxide can cause complete saponification of methyl stearate to sodium stearate and methanol when used in equimolar quantities. When adding sodium hydroxide to the immiscible glycerol and methyl stearate at 130 C, a single-phase system was formed after 5 min of mixing. Follow-up of this reaction showed that methyl stearate was consumed gradually, forming monoglyceride and diglycerides of stearic acid. Transesterification was much slower when the reaction was done in the presence of sodium stearate and the absence of sodium hydroxide. The presence of both sodium hydroxide and sodium stearate proves to have the best effect on the methyl stearate consumption and on the formation of mono- and diglyceride. A transparent, one-phase system was observed during the transesterification reaction.

A few tests have been done to verify the formation of an emulsion or microemulsion: (a) the addition of water- or oil-soluble colorants have proven that the external continuous phase is methyl stearate and the internal phase is glycerol (glycerol in oil emulsion). (b) Upon "diluting" the system with additional methyl stearate, no separation of phases appeared. However, "diluting" the system with glycerol caused opacity and further dilution caused a separation of the two phases (breaking of the emulsion). (c) Microscope examination of these emulsions revealed that few of the droplets were in the range of 0.5 μ, which means that formation of a microemulsion has been achieved, (0.01-0.05 μ). Additional indication for the existence of an emulsion system was obtained by using tetraglycerol instead of monoglycerol (glycerol). Tetraglycerol is completely immiscible with methyl stearate at low and high temperatures. Upon addition of an adequate emulsifier, an emulsion is formed consisting of droplets in the range of 0.5-5 μ. When the amount of the methyl stearate or the emulsifier concentration is increased, and/or the temperature, the macroemulsion is transformed into a micro-emulsion with droplet size of 0.01-0.5 μ.

Effect of Reactants' Ratio

According to Osipow and Rosenblatt's previous report (5), the reaction between glycerol and methyl oleate was done in an excess of glycerol (usually twice the molar ratio of methyl oleate). In our study, the formation of an emulsion requires an excess of methyl stearate serving as the continuous phase in glycerol or polyglycerol in oil emulsion. Thus, it has been found that, to form a more stable emulsion with higher conversions, a relatively high concentration of methyl stearate should be used.

The effect of the reactants' ratio on the yield of the reaction and the product distribution is summarized in Table I.

The polyol-to-methyl stearate ratio has been varied from 0.25 to 3.0 and the reaction conversion was evaluated by determining the methyl stearate consumption. When tetraglycerol was used, it was found that the conversion of methyl stearate to the tetraglycerol esters was improved by increasing the polyol concentration, and higher selectivity toward the monoester was obtained. At ratios of 0.3 and 0.25 (reactions 10 and 11, respectively), the selectivity is very low and the product consists mostly of tetraglycerol distearate (24.4 and 9.6%) and tetraglycerol tristearate (36.8 and 51.0%) and only 8.9 and 2.4% of tetraglycerol monostearate were formed. At ratios of 2.0 (reaction 7), the product consists of 58.9% of tetraglycerol monostearate and only 1.3% of the diesters. But, the amount of the active emulsifier is higher at low ratios of tetraglycerol to methyl stearate. Similar results were obtained when glycerol served as the polyol. At high glycerol-methyl stearate ratios, the conversion of methyl stearate is up to 91.1% (reaction 4) but only 57.3% methyl stearate was consumed (reaction 6) at a ratio of 0.3.

In all procedures, emulsions were formed and kept stable throughout the reaction. Yet, in reactions 2, 3, 7 and 8, immediate separation of a polyol phase was observed after cooling the product due to the presence of excess polyol in

TABLE I

Effect of Reactants Ratio on the Conversion of Methyl Stearate and the Reaction Selectivity [a]

Reaction no.	Polyol/methyl stearate (molar ratio)	Methyl stearate conversion (%)	Monoester formation (% of total product)	Monoester (% of the esters product)	Mono/diester (molar ratio)
Glycerol					
1	3[b]	99.5	25.1	49.9	1.00
2	3	86.1	37.1	72.3	5.31
3	2	83.5	33.5	60.7	2.69
4	1	91.1	25.7	36.3	0.99
5	0.5	78.1	18.1	26.8	0.64
6	0.3	57.3	9.4	18.4	0.39
Tetraglycerol					
7	2	100.0	58.9	97.9	67.7
8	1	89.2	39.0	56.2	1.87
9	0.5	83.9	21.3	27.2	0.59
10	0.3	74.4	8.9	12.66	0.53
11	0.25	66.8	2.4	3.9	0.37

[a]10 wt % (of the oil phase)—Na-stearate; 0.15 % NaOH; 130 C; 8 hr.
[b]30 wt % of Na-stearate.

the inner phase, which caused instability of the emulsions formed.

Reaction 1 was done at the same reaction conditions, but in the presence of 30 wt % Na-stearate. A stable microemulsion was formed and did not break, even at the end of the reaction after cooling. All other reactions showed no separation of polyol because most of it reacted, and the small quantities left were in stable emulsions which did not break.

Type and Amount of Emulsifier

The amount of emulsifier (Na-stearate) has a pronounced effect on the droplet size of the emulsion and on its stability. The larger the amount of emulsifier, the higher the stability, resulting in increased consumption of methyl stearate. Results are summarized in Table II.

Without an emulsifier (reaction 17) there is no methyl stearate consumption. Since 0.48 wt % Na-stearate caused a limited contact between the reactants, only 5.2% of methyl stearate converted to tetraglycerol monostearate. With 6.8 wt % Na-stearate there is a 100% conversion of methyl stearate to tetraglycerol esters. But the selectivity is lower with high emulsifier concentration because of a better contact between the reactants. Therefore, more of the diesters are formed, consuming the monoesters. When 2.4 wt % emulsifier formed a stable macroemulsion, 26.7% of tetraglycerol monostearate and 11.2% of tetraglycerol distearate were produced. A microemulsion can be observed with 6.8 wt % emulsifier—42.9% of tetraglycerol monoesters and 33.1% of tetraglycerol distearate were formed.

Similar behavior was found with glycerol. Only 9.6% of methyl stearate was converted to give 8.7% of glycerol monostearate. With 0.75 wt % Na-stearate, no formation of diester was observed. A 100% conversion was achieved with 10.3 wt % Na-stearate, yielding 27.6% of glycerol monostearate and 47.6% of glycerol distearate. This reaction showed very low selectivity.

Emulsification of methyl stearate and polyols can be obtained either by nonionic, anionic or cationic emulsifiers. Table III summarizes part of the results obtained for various emulsifiers.

When nonionic emulsifiers are used, the transesterification of methyl stearate is between 0-20.8% as a result of

low emulsion stability. For example, emulsifiers such as Span 40 and Span 20 could not stabilize the emulsion; therefore, no methyl stearate was consumed with these emulsifiers.

Ionic emulsifiers were found to be much more effective, as can be seen from the methyl stearate conversion which is up to 83.9-98.1% for anionic emulsifiers, and 56.8-72.7% for CMAB, a typical cationic emulsifier. Na-stearate allows conversion of 83.9% of methyl stearate when it is treated with tetraglycerol. However, due to low solubility in both phases, Mg-stearate or Ca-stearate converted only 17.9 and 2.9%, respectively, of the methyl stearate.

Investigators (8,9) have reported that inorganic salts such as $MgSO_4$, $MgCO_3$ and others can serve as surfactants, facilitating formation of an emulsion. In our system, alkaline inorganic salts were used both as catalysts and as emulsifiers. The immediate formation of an emulsion and the high methyl stearate conversion—up to 98.1% (with Na_2CO_3)—point to the double function of the carbonates.

Effect of Temperature

The rate of methyl stearate consumption as a function of temperature has been examined. The emulsion stability improved significantly, and as a result, the conversion of the methyl stearate to the esters increased. (See Table IV.)

For tetraglycerol, as the temperature increased, the quality of the emulsion improved. Upon turning of the stirring at 110 C, the emulsion breaks. At elevated reaction temperatures, the emulsions previously formed remain stable, even when the stirring stops or at the end of the reaction. The conversion of the methyl stearate increased from 49.7% at 110 C to 100% at 150 C. The behavior with glycerol is even more pronounced: at 95 C, the conversion is only 14.9% and reaches 100% at 140 C.

For glycerol, the amounts of glycerol mono- and distearates are 12.7 and 0.06%, respectively, at 95 C, and at 150 C, 31.5% of glycerol monostearate and 46.7% of glycerol distearate are formed, expressing loss of selectivity at high temperatures. With tetraglycerol, the same behavior was found. But since the molar concentration of the methyl stearate was twice the molar concentration of the tetraglycerol, at low temperatures (100 C-120 C), the tetraglycerol monostearate content increased from 14.6% (at

TABLE II

Effect of Emulsifier Concentration on the Methyl Stearate Conversion and Mono- and Diesters Formation[a]

Reaction no.	Na-stearate (wt %)	Methyl stearate conversion (%)	Monoester (% of total product)	Monoester (% of the esters product)	Mono/diesters (molar ratio)
Glycerol					
12	0.75	9.6	8.7	100	—
13	1.89	33.5	15.7	55.4	2.17
14	3.7	73.2	24.5	41.0	1.18
15	7.1	91.1	25.7	36.3	0.57
16	10.3	100.0	27.6	36.8	0.58
Tetraglycerol					
17	—	—	—	—	—
18	0.48	5.2	4.9	100	—
19	1.20	25.4	16.1	74.2	4.16
20	2.4	45.5	26.7	70.4	3.48
21	4.6	89.2	38.9	56.2	1.87
22	6.8	100.0	42.9	56.4	1.29

[a]Polyol/methylstearate = 1:1; 0.15% NaOH; 130 C; 8 hr.

TABLE III

Effect of Emulsifier Type on the Methyl Stearate Conversion[a]

Nonionic emulsifiers	HLB	Methyl stearate conversion (%)		Ionic emulsifiers	Methyl stearate conversion (%)	
		Tetraglycerol	Glycerol		Tetraglycerol	Glycerol
Tween 80	15.0	20.8		Na-stearate	83.9	91.1
Tween 60	14.9	0	19.5	Mg-stearate	17.5	
				Ca-stearate	2.9	
Span 80	4.3	5.5				
Span 60	4.7	0	5.7	Na_2CO_3	98.1	
Span 40	6.7	0		K_2CO_3	97.2	
Span 20	8.6	0		$MgCO_3$	84.9	
				$CaCO_3$	87.2	
Brij 72	4.9	6.73		CMAB	56.8	72.7
MDG	2.8	4.8				
3G10	8.8	15.5				

[a]10 wt % (of the oil phase) of emulsifier; 0.15% NaOH; 130 C; 8 hr; tetraglycerol/methyl stearate = 2:1; glycerol/methyl stearate = 1:1

TABLE IV

Effect of Reaction Temperature on the Methyl Stearate Conversion and the Reaction Selectivity[a]

Reaction no.	Temperature (C)	Methyl stearate conversion (%)	Monoester (% of total product)	Monoester (% of esters product)	Mono/diester (molar ratio)
Glycerol					
23	95	14.9	12.7	99.5	3.55
24	110	21.6	15.3	85.1	9.96
25	120	75.5	21.7	36.9	1.02
26	130	91.1	25.7	36.3	0.99
27	140	100	28.3	36.4	1.00
28	150	100	31.5	40.3	1.18
Tetraglycerol					
29	100	23.2	14.6	60.4	2.22
30	110	49.7	25.1	50.1	1.47
31	120	68.2	30.7	45.2	1.20
32	130	83.9	21.3	27.5	0.59
33	140	96.0	19.6	23.0	0.77
34	150	100.0	14.8	16.9	0.49

[a]10 wt % (of the oil phase)-Na-stearate 0.15% NaOH; 8 hr; glycerol/methyl stearate = 1:1; tetraglycerol/methyl stearate = 1:2.

100 C) to 30.7% (at 120 C). Further increase in the temperature caused a decrease in the monoester content, because more of the diester had to be formed—up to 65.6% at 150 C.

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