Micro-Emulsion Process for the Preparation of Sucrose Esters[1]

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Abstract

A new process, based on micro-emulsion technology, has been developed for the production of sucrose esters of fatty acids. Sucrose dissolved in propylene glycol, methyl stearate, sodium stearate, and catalyst (K_2CO_3) are combined to form a transparent emulsion and interacted. The system remains transparent throughout the distillation of the propylene glycol, indicating the formation of a micro dispersion of sucrose. Upon completion of the distillation all of the methyl stearate is converted to sucrose stearate. Starting with a 1.5:1.0:0.9 molar ratio of sucrose, methyl stearate, and sodium stearate, the reaction product, after purification, is 85% sucrose monostearate, 15% sucrose distearate.

Introduction

THE FIRST PAPER describing a practical commercial process for the preparation of sucrose esters of fatty acids appeared in 1956 (1). This process involved a transesterification reaction between sucrose and the methyl ester of a fatty acid in the presence of basic catalyst and mutual solvent, such as dimethylformamide. The sucrose esters are now produced on a semicommercial scale in several countries, including the United States. However the volume of production is far less than had been anticipated, because of both the cost of solvent lost during processing and the high cost of purifying the sucrose esters to remove traces of solvent and obtain an edible emulsifier.

This paper is concerned with a new process that was developed to avoid the difficulties characteristic of the older one. This involved the formation of a micro emulsion instead of the use of a mutual solvent.

Micro Emulsions

The conventional emulsions that are widely used in the home and in industry are opaque, with droplet diameters generally in the range of 1 to 10 μ. In contrast with these macro emulsions, micro emulsions can be readily produced with the diameter of the droplets in the range of 0.01 to 0.06 μ. Since the diameter of the droplets is less than one-fourth of the wavelength of light, the emulsions are transparent.

Bowcott and Schulman (2) showed that, in order to form micro emulsions, it is necessary that the concentration of emulsifiers be greater than that required to reduce the oil-water interfacial tension to zero. This indicates that the interfacial tension must have a metastable negative value, which would give a negative free energy variation. This would cause droplets to break up spontaneously, stabilize the dispersed phase, and prevent phase separation. Micro emulsions are thermodynamically stable.

Micro emulsions can be formed by using aqueous solutions which contain 10 to 40% of ionic surfactant. In these concentrated solutions the surfactant micelles have a definite lamellar structure which can be swelled to only a limited extent by nonpolar oils. Above the Krafft temperature these lamellar micelles are completely dispersible in water. When these micelles are penetrated by amphiphilic molecules (lyophilic-lyophobic), such as medium-chain alcohols, they are able to swell almost without limit with both oil and water as long as there is a condensed interphase.

The lamellar structure may be considered as an interphase between oil and water. If sufficiently fluid, surface-tension forces will produce a curvature according to the difference in tension between the hydrocarbon portion of the interphase molecules and the oil phase and between the hydrophilic portion of the interphase molecules and the water phase. The effect of the formation of a mixed interfacial film containing the water-soluble ionic surfactant and the oil-soluble amphiphilic molecule is to lower the interfacial tension between the oil and water phases to only a fraction of a dyne/cm. A micro emulsion will form if the interface is liquid and can be penetrated by the oil. In the case of a hydrocarbon oil the chain length of the hydrocarbon oil must not exceed the chain length of the components of the mixed interfacial film. If the interfacial film is too strongly condensed to be penetrated by oil molecules, it will not be able to assume a large enough curvature to form droplets below about one micron diameter (3).

The phase continuity of micro emulsions is governed by the same factors as macro emulsions. If the emulsifying agent is not ionized and is preferentially soluble in the oil phase, the emulsion will be water-in-oil. If it is not ionized and is preferentially soluble in water, the emulsion will be oil-in-water. If the interfacial film is charged, the emulsion will be oil-in-water (3).

Application to Transesterification

There are occasions where it is necessary to react two immiscible materials and it is inadvisable to use a mutual solvent. A case in point is the reaction between sucrose and a fatty ester to form the sucrose ester of the fatty acid. A number of attempts have been made to carry out this reaction, without a mutual solvent, using either finely ground sugar or an emulsion. At best, only detectable amounts of sugar ester were recovered.

It appeared reasonable that greater success could be achieved by forming a micro emulsion since the droplet size in micro emulsions approaches molecular dimensions.

Insofar as the authors have been able to determine, no one has previously examined the possible use of micro emulsions as a method for organic synthesis. The sucrose ester reaction is too complex to consider initially in determining whether a micro emulsion procedure would actually work.

A more ideal system for initial study is the reaction between glycerine and a triglyceride or a methyl ester of a fatty acid to form a monoglyceride. At moderate temperatures the reactants are liquid and

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TABLE I

Reaction of Glycerine with Methyl Oleate for 5 hrs at 110C, Using 0.1% Sodium Methoxide as Catalyst. A Micro Emulsion Formed in the Last Two Reactions.

Glycerine (moles)	Methyl oleate (moles)	Sodium oleate (moles)	Product	
			Hydroxyl number	Estimated monoglyceride content
1.08	0.33	0.0	3.0	....
1.08	0.33	0.017	32.9	....
1.08	0.33	0.03	107.4	7.5%
1.08	0.33	0.06[a]	220.3	57.8%
1.08	0.33	0.13	210.6	53.7%

[a] Emulsion was hazy.

practically insoluble in each other. Formation of monoglyceride is ordinarily carried out by heating, in the presence of an alkaline catalyst, to about 200–250C. In this temperature range there is sufficient solubility of glycerine in the fat to give an equilibrium mixture of mono-, di-, and triglycerides containing about 50% of monoglycerides.

The concept of employing a micro emulsion for an organic synthesis was tested with the monoglyceride reaction at 110C. A coarse emulsion was maintained by vigorous agitation of the reactants and alkaline catalyst for three hours. A comparison experiment was carried out in the same manner except for the addition of sufficient soap to form a micro emulsion. Practically no monoglyceride was formed with the crude emulsion while up to about 75% of monoglyceride was produced by using a micro emulsion. This seemed to confirm the validity of the concept.

To form a sucrose ester it is not possible simply to substitute sucrose for glycerine. Sucrose does not melt and cannot be emulsified. It is necessary to dissolve the sugar prior to forming an emulsion. There are few good solvents for sucrose that are also edible. Propylene glycol was selected. This solvent however contains hydroxyl groups and will compete with sucrose in the transesterification reaction. Further, since more propylene glycol than sucrose is used to prepare the solution, more propylene glycol ester than sucrose ester should be present at equilibrium.

It should be possible to shift the equilibrium toward sucrose ester formation by distilling off the propylene glycol. This could not occur if sucrose crystallized out of solution as the propylene glycol was distilled. Macro crystals cannot react at any reasonable rate. Instead it is necessary that the sucrose precipitate in micro-dispersed form. The sucrose particles should be of the same relative size as micro-emulsion droplets.

Thus the requirements for the formation of sucrose ester according to the micro-emulsion concept are as follows. First, it must be possible to form a micro emulsion between a fatty ester and a solution of sucrose in propylene glycol. Second, the micro emulsion must be maintained during the distillation of the propylene glycol. Third, sucrose must precipitate during the distillation of solvent in a micro-dispersed form in order to retain its reactivity. Results obtained with sucrose and fatty esters bear out the validity of the micro-emulsion concept.

TABLE II

Reaction of Glycerine with Glyceryl Trioleate for 6 hrs at 110C, Using 0.1% Sodium Methoxide as Catalyst. A Micro Emulsion Formed in all but the First Reaction.

Glycerine (moles)	Glyceryl trioleate (moles)	Sodium oleate (moles)	Product	
			Hydroxyl number	Estimated monoglyceride content
1.08	0.11	0.0	4.0	......
1.08	0.11	0.06	219.9	57.8
1.08	0.11	0.13	243.6	68.5
1.63	0.08	0.13	256.2	73.8
1.63	0.08	0.26	258.9	75.0

Materials. These were glycerine U.S.P., 99.5%, and methyl oleate: Humko Division, National Dairy Products Inc.; methyl stearate (Metholeen 2218, normally 95% stearate, 4% palmitate, 1% oleate): Emery Industries Inc.; propylene glycol U.S.P.: Union Carbide Corporation; triolein, tech.: Matheson, Coleman and Bell Division, Matheson Company; sodium oleate, purified, and sodium stearate, technical: Fisher Scientific Company. All materials were used without purification.

Preparation of Monoglycerides. The reactions were carried out in a three-necked flask, equipped with a thermometer, motor-driven stirrer, and an adapter for vacuum. The appropriate amounts of glycerine, sodium oleate, and either methyl oleate or glyceryl trioleate were placed in the flask and heated for two hours at 110C/5 mm Hg. to remove any water that might be present. The vacuum was then momentarily released, and sodium methoxide was added. The reaction mixture was maintained at 110C/5 mm Hg. for three or four additional hours.

The product was recovered by dissolving in diethyl ether and washing repeatedly with an aqueous solution of sodium sulfate to remove glycerine. The ether extract was dried over anhydrous sodium sulfate, and the ether was removed by distillation.

The monoglyceride content of the product was estimated from the equation: $315\,X + 90.5\,(1 - X) =$ Hydroxyl number of product where 315 is the hydroxyl number of pure glyceryl monooleate, 90.5 is the hydroxyl number of pure glyceryl dioleate, X is the weight fraction of monoglyceride in the product, and $1 - X$ is the weight fraction of diglyceride.

Table I shows the results obtained in a series of runs by using methyl oleate. Without soap or with insufficient soap to form a macro emulsion little monoglyceride formed. When sufficient soap was present to form a micro emulsion, the yield of monoglyceride was greatly increased. A further increase in soap content, beyond that required to form the micro emulsion, did not increase the yield of monoglyceride.

The results of a similar series of experiments using glyceryl trioleate are shown in Table II. No reaction occurred in the absence of soap but, when the reactants were combined as a micro emulsion, the products contained more than 50% of monoglyceride. Comparison of the third and fourth reaction shows that increasing the ratio of glycerine to triolein shifts the equilibrium between glycerides to give a higher yield of monoglyceride. Comparison of the second with the third reaction and the fourth with the fifth reaction shows in one instance an improved yield of monoglyceride by doubling the soap content but not in the second case.

To the extent that increasing the soap content decreases the size of the micro-emulsion droplets, an increase in the reaction rate would be expected. The effect on the equilibrium between mono-, di-, and triglycerides is more complex and will depend upon the distribution of the components between the phases.

It may be noted that the amount of soap required to form the micro emulsion provides sufficient alkalinity to catalyze the transesterification reaction, and sodium methoxide is not required.

Preparation of Sucrose Esters

The following illustrates the preparation of sucrose monostearate. The reaction is carried out in a two-liter resin kettle, fitted with a thermometer, stirrer, and water-jacketed condenser and connected to a receiver which leads to a vacuum source.

Introduce into the resin kettle 900 ml of propylene glycol, 308.4 g (0.90 mole) of sucrose, 180.0 g (0.60 mole) of methyl stearate, 165.0 g (0.54 mole) of sodium stearate, and 1.0 g of anhydrous potassium carbonate. Heat with stirring to 130–135C. In this temperature range the sugar will dissolve completely and the reaction mixture will be clear and homogeneous. Apply vacuum, and begin the distillation of the glycol, maintaining the temperature above 120C.

It is necessary gradually to increase the temperature during the distillation of the glycol otherwise turbidity develops and the reaction does not go to completion. Turbidity is first observed after 30 to 40% of the glycol is distilled. The emulsion clarifies at 145–150C/130–140 mm Hg. In the final stage of the distillation the glycol is completely removed at 165–167C/3–4 mm Hg. The reaction mass can be removed from the kettle while it is still fluid. At room temperature it is friable and can be easily crushed and ground.

Table III shows the composition of the reaction mix per 100 g of solids and the composition of the solids after completion of the reaction.

A purified product can be obtained by taking up the ground mixture in hot methyl ethyl ketone and filtering to remove the sugar and most of the soap. The solution is then acidified to convert dissolved sodium stearate to stearic acid, cooled, and refiltered to recover the sugar ester as a filter cake. Typically the product recovered after solvent removal is about 96% sucrose ester and about 2% each of fatty acid and salt. As determined by optical rotation and by hydrolysis, the sucrose esters run about 85% monoester, 15% diester.

Discussion

There are several interesting aspects to the micro-emulsion process. Soap at a pH of above 10 cannot be used to form a micro emulsion in water without the addition of a fatty alcohol or other amphiphilic molecule. A micro emulsion can be formed in water at lower pH levels because of the presence of free fatty acids. Alkaline soap alone will form a micro emulsion in propylene glycol, presumably because the soap is ionized to a lesser extent in the nonaqueous solvent. Further the micro emulsion only exists at the elevated temperature, and it becomes opaque on cooling, indicating the transition from a liquid to a solid interfacial film.

As indicated by miscibility tests, the propylene glycol solution is the continuous phase in the micro emulsion. If it were the discontinuous phase, it would be easy to understand why the sugar does not precipitate as macro crystals during the distillation. The micro droplets of sugar solution would simply decrease in size as the propylene glycol was distilled, and the soap film would keep the micro crystals of sucrose from growing together. Presumably, even with the propylene glycol solution as the continuous phase, the high content of soap is sufficient to interfere with the growth of sucrose crystals. The possibility that there is a phase inversion during the distillation of propylene glycol has not been examined.

TABLE III

Reaction mix per 100 g of solids	
Sucrose	47.2 g
Methyl stearate	27.6 g
Sodium stearate	25.2 g
	100.0 g
(+ 137 ml of propylene glycol)	
Product mix *from 100 g of solids*	
Sucrose stearate	53.9 g
Sucrose	19.5 g
Sodium stearate	25.2 g
	98.6 g
(+ 1.4 g methanol distilled)	

Of practical importance is the observation that about an 85:15 weight ratio of sucrose monoester to sucrose diester is obtained by using a 1.5:1.0 molar ratio of sucrose to methyl ester in the micro-emulsion reaction while a 3:1 molar ratio of sucrose to methyl ester is required to give the same product distribution in the solution reaction. The presence of the reactants in separate phases as well as the possibility that the soap forms mixed micelles with the sucrose monoester and acts as a physical barrier to hinder further reaction may be contributing factors.

The micro-emulsion reaction for the preparation of sucrose esters offers a number of advantages over the solvent reaction, as follows. Less excess sucrose is used. The solvent is recovered quantitatively during the reaction. The solvent is edible and does not form toxic products during the reaction; residues remaining in the product are not a barrier to its use in food applications. The only significant losses that occur are on account of the caramelization of the sugar, and this is only about 10% of the initial sugar content. Recovery of the sucrose ester product in purified form is uncomplicated.

It is anticipated that this new procedure for the preparation of the sucrose esters will permit a substantial expansion in the production and utilization of these surfactants.

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