Influence of Temperature-Induced Phase Transitions on Fat Emulsions


ABSTRACT

The polymorphic behavior of a commercial monoglyceride emulsifier together with a liquid vegetable oil and water has been investigated by means of microscopic examination and differential scanning calorimetry. The results show that the stability regions of the liquid crystalline phases formed are highly dependent on the temperature and related both to the solubility of the monoglyceride emulsifier in the oil phase and to its polymorphic behavior. The formation and stability of emulsions are discussed in connection with the results obtained.

INTRODUCTION

The properties of fat emulsions depend to a high degree on the temperature during the pretreatment and mixing of the ingredients. It is our opinion that this is due to temperature dependent changes involving the crystalline and liquid crystalline phases which occur in fats and in lipid emulsifiers. Furthermore these changes show marked hysteresis phenomena and nonreversible behavior which can give rise to problems when processing emulsified products on a factory scale.

The phase behavior of aqueous systems of monoglycerides with chain length ranging from C12 to C22 has been studied by Lutton (1) who identified mesophases of the neat, viscous isotropic and middle structure. An extensive study at different temperatures of the phase behavior of a series of aqueous monoglyceride systems with chain length down to C6 was made by Larsson (2). The presence of seven liquid crystalline and micellar phases was shown. In particular a reversed middle phase was observed to be formed either by monoglycerides with long chain fatty acids or by combination of monoglycerides with diglycerides of the same fatty acid. This structure consists of hexagonally arranged cylinders of water surrounded by lipids. In an investigation by Krog and Larsson (3) of water mixtures of monoglycerides prepared from natural fats, the practical importance of the lamellar structured phase, called dispersion, in emulsion formation was emphasized. X-ray diffraction showed the occurrence of two crystalline forms, the metastable \( \alpha \)-form and the stable \( \beta \)-form.

The determining influence of liquid crystalline phases on stability (4) and viscosity of emulsions (5) has been shown at our institute in a series of investigations on phase equilibria at 20 \( ^\circ\)C in three-component systems.

In view of the importance of emulsions in food technology we have investigated the polymorphic behavior and the degree of reversibility of phase transitions in a system of a commercial monoglyceride in combination with water and liquid oil.

EXPERIMENTAL PROCEDURES

The monoglyceride (DMG) was a commercially available product produced by molecular distillation of a mixture of mono-, di- and triglycerides obtained from interesterification with glycerol of a fully hardened soy bean oil. The monoester content was 94\%, of which glyceryl monooleate was the main component together with minor amounts of other fatty acid monoglycerides (Fig. 1).

The triglycerides were derived from industrially refined liquid soy bean oil (SBO). The water was distilled twice.

All samples were observed grossly by polarizing microscope, melting point estimations and by differential scanning calorimetry (DSC).

The monoglyceride sample was mixed with water or soy bean oil in concentration intervals of 5\%. Mixtures of 5 g were prepared in ampoules and heated to obtain isotropic

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1Presented at the ISF-AOCS World Congress, Chicago, September 1970.

THREE-COMPONENT SYSTEM

<table>
<thead>
<tr>
<th>DISTILLED WATER (W)</th>
<th>IND. DISTILLED MONOGLYCERIDE (DMG) 94%</th>
<th>COMMERC. TRIGLYCERIDE (SBO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acid comp:</td>
<td>ref. liq.</td>
<td>soybean oil</td>
</tr>
<tr>
<td>( C_{16} )</td>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>( C_{18} )</td>
<td>85%</td>
<td></td>
</tr>
<tr>
<td>( C_{20} + C_{22} )</td>
<td>6%</td>
<td></td>
</tr>
<tr>
<td>others</td>
<td>2%</td>
<td></td>
</tr>
<tr>
<td>mp ( 72-74 ^\circ)C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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FIG. 1. Specifications and terms for the components used in the investigation.

FIG. 2. SBO-DMG binary phase diagram. Line A: the melting curve for DMG crystals when slowly crystallized in SBO solution. Line B: the melting curve for the \( \beta \)-crystals when the solution has been rapidly cooled below line C and stored at room temperature for 18 hr. Line C: the solidification temperatures of the \( \alpha \)-form for the solid solution of SBO-DMG obtained by rapid cooling. Line D and E: the solidification temperatures of the \( \alpha \)-form of the solid solutions when 5 and 10\% water, respectively, is solubilized.
solutions. For rapid cooling ampoules were placed in a water bath at room temperature and then in a thermostatically controlled bath at the required temperature previously determined to be in the vicinity of a phase transition point. For slow cooling the ampoules were placed in an insulated water bath at 90°C which was allowed to slowly cool down to the required temperature. The ampoules were centrifuged at this temperature and the homogeneous content or the separated layers were investigated by microscopy, melting point estimations and DSC measurements. Small samples of the mixtures were also directly tempered on slides on the microscopic stage, in the melting capillaries or in the small pans for the DSC.

**Microscopic Examination**

The samples were examined by a polarizing microscope, Leitz Orthoplan, fitted with a special heating-cooling stage, thermostated to an accuracy of ±1°C. To ensure good thermal contact with the heating-cooling stage, samples were placed on thin glass slides, 0.16 mm thick. The different liquid crystalline phases were optically identified. The temperatures at which phase transitions occurred were determined by approaching the transition points both from higher and lower temperatures. Each sample was studied in duplicate or triplicate. Photographs were taken in polarized light and with a “1st-order red” plate as compensator.

**Capillary Melting Point**

Besides the microscopic examination of melting and transition points, the instantaneous melting point test (6) was used to estimate the melting point of the phases when solidified in the unstable α-form. A slip-point test after a tempering period of 18 hr was used for the determinations of β-form melting points.

**Differential Thermal Analysis**

Perkin Elmer DSC was used. The samples were 2-4 mg and heated at a rate of 4°C/min until phase transformations were observed. The method was used to check the transition and melting points found by microscopic examination or capillary melting point estimation.

**RESULTS**

**DMG-SBO**

On addition of SBO both the melting and solidification temperatures of the DMG are reduced. The reduction is small for additions of less than 50% SBO, but increases rapidly at higher amounts (Fig. 2). In accordance with the polymorphic behavior of pure glycerides, the DMG-SBO solutions solidified in two modifications, the low melting unstable α-form and the higher melting stable β-form. When rapidly cooled the α-modification is formed, and this transforms readily in solid state to the β-modification (Fig. 3). Slow cooling of DMG-SBO solutions causes a crystallization in the β-form of the fairly insoluble DMG. When water is added further depression of the crystallization temperature of the α-form occurs, and this depression is independent of the initial amount of SBO. Up to 10% water can be solubilized when the ratio to DMG in SBO is high.

**DMG-Water**

The general form of this phase diagram (Fig. 4) is similar to earlier published results (1-3). Besides the neat, viscous and fluid isotropic phases previously reported in commercial DMG-samples and described as monostearins, we also found a reversed middle phase. This phase can likely be accounted for either by the presence of fatty acid chains longer than eighteen carbon atoms or by the presence of