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The phase behaviour of mixed saturated and unsaturated monoglycerides in water system

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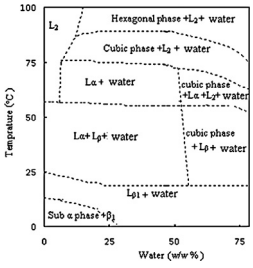
HIGHLIGHTS

- The phase behaviour of mixed monoglycerides in water system has been investigated.
- The phase diagram shows three bicontinuous cubic phases.
- The swelling of head group progressed up to 50% of water.

GRAPHICAL ABSTRACT



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ABSTRACT

Lyotropic liquid crystalline phases are formed over a limited range of surfactant concentrations and temperatures as represented by regions on the phase diagram. Acknowledgement of the surfactant phase diagram is a major step in developing any industrial application. In this work; we have examined the phase behaviour of mixed saturated and unsaturated monoglycerides 1:1 (by weight) together with water. The main technique employed was X-ray diffraction, supplemented by optical microscopy and differential scanning calorimetry (DSC). The phase diagram which is a novel finding shows six phases for GMS/GMO mixture without water: α-gel (Lβ) phase, new α-gel (Lβ1) structure, β1 crystal phase, sub-α phase, β2-crystal, as well as an isotropic, L2, phase. In the presence of water five additional phases are formed, fluid lamellar phase, three bicontinous cubic phases, Ia3d, Pn3m and Im3m with increasing the water content, and on further heating all bicontinous cubic phase convert to a hexagonal phase. Our results show that the maximum swelling capacity of the mixture of monoglycerides in water is obtained at 50% (w/w) water content, and there are important differences in the phase behaviour between mixed saturated and unsaturated monoglycerides with and without water.

1. Introduction

Monoglycerides have significant mesomorphic behaviour due to their amphiphilic structure. In the presence of water, at temperatures above the melting point of the hydrocarbon region, the hydrocarbon chains transform into a disordered state and water penetrates into the ordered polar groups [1].

The phase behaviour of saturated monoglyceride (GMS) and unsaturated monoglyceride (GMO)/water systems has been extensively studied [1–8]. The α-gel (L_β), lamellar (L_α) and bicontinuous cubic (V_2) mesophases are commonly observed for the saturated monoglyceride/water system [9]. However, systems containing unsaturated monoglycerides form the lamellar phase (L_α), bicontinuous cubic phase (V_2) and inverse hexagonal phase (H_2) [1,9]. More than one type of cubic phase and two separate hexagonal

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phases are formed by the monoglycerides/water system [10,11]. The long chain saturated monoglycerides form a highly hydrated lamellar phase above a certain critical temperature [12]. When the lamellar phase is cooled the α-gel phase is formed, which eventually transforms to an anhydrous crystalline phase (the "coagel") [13,14].

The head groups in the lamellar phase are more hydrated than in the α-gel phase. This reduced hydration is probably attributable to the ordered alkyl chain array of gel phase, which forces the head groups closer together than in the lamellar phase. The swelling capacity of the aqueous lamellar phase of non-ionic monoglycerides is limited by the long range van der Waals forces between the lipid bilayers [15]. However, introducing charged groups to the bilayer increases the electrical double-layer repulsive forces so swelling can proceed and the lamellar phase expands into the higher water content region [16]. If the water content is increased above the swelling limit of the lamellar phase, a lamellar dispersion can be formed [1]. The ability of monoglycerides to swell in water and to form stable interfaces with a lamellar structure between oil and water has been found to be important for emulsion stability [17]. However, little information is available regarding the ternary phase behaviour of monoglyceride–oil–water systems [18,19]. Salonen et al. [20] investigated the determination of the water content in the GMO–oil–water system. Yaghmur studied in detail the discovery of Fd3m phase (reversed discontinuous micellar cubic), which is formed in the monolinolein–water–tetradecane system at a specific tetradecane/monolinolein weight ratio. It is situated between the H_2 and the isotropic liquid phase [21].

Recent work on this ternary phase behaviour has shown that lamellar phase walls surround oil droplets. These walls are continuous from one oil droplet to the next, thereby forming a continuous solid network to retain the solvent inside [18]. Calligaris et al. [22] studied the aroma release properties of monoglyceride–oil–water gels. The results demonstrated that the lamellar phases affect the partition of aroma confirming the ability to entrap lipophilic compounds within the monoglyceride–oil shells. This could affect the perceived aroma intensity of the final product [22]. Amar-Yuli and Garti [23] examined the effect of triglycerides of different chain lengths (C2, C8 and C18) on phase transitions of GMO from lamellar or cubic to reverse hexagonal (L_α–H_2 and Q–H_2). The H_2 mesophase is stabilised with tricaprylin over the cubic phase and L_α phases. It was found that triacetin (water soluble) does not affect the mesophase structures, while tristearin does not dissolve (hence has zero effect) [23]. Some data were also reported for the effects of added NaCl, which also promoted the stability of the H_2 phase.

In the food industry, there is considerable interest in the behaviour of mixed monoglycerides in water but no information is available for mixed monoglyceride/water systems. Therefore, the effects of added water on the phase behaviour of mixed monoglyceride have been investigated. Recently various phases for GMS/GMO mixtures were reported by us [24]. The α-gel (L_β) phase, a new α-gel ($L_{\beta 1}$) structure, a β_1-crystal phase, a sub-α phase, a β_2-crystal, as well as an isotropic, L_2, and two forms of β-crystals were observed. The β_1 phase was formed by GMO crystallisation and the β_2 phase by ageing of GMS. Additionally, two types of gel phase were observed in the mixture; the new type of the α-gel structure in the mixture has a more disordered structural arrangement and cannot pack in the same hexagonal structure as the α-gel phase formed by saturated lipids [24].

We have examined the phase behaviour of mixed saturated and unsaturated monoglycerides 1:1 (by weight) in water using various methods. Optical microscopy was used to study the phase behaviour as a function of temperature. We also employed differential scanning calorimetry (DSC) to determine the transition enthalpies between phases. In parallel, we used small angle X-ray scattering (SAXS) to characterise the different phases at different temperatures.

Table 1
Nomenclature.

Nomenclature	Phase name	Packing modes
L_2	Isotropic phase	Disordered
L_α	Lamellar phase	Disordered
Sub-α phase	Sub-α phase	Orthorhombic lattice
L_β	α-gel phase	Hexagonal lattice
$L_{\beta 1}$	New structure of α-gel phase	Hexagonal lattice
β_1-crystal	GMO crystal	Triclinic lattice
β_2-crystal	GMS crystal	Triclinic lattice
V	Cubic phases	Cubic lattice
H_2	Reversed hexagonal phase	Reversed hexagonal lattice

Our results suggest that there are important differences in the phase behaviour between mixed saturated and unsaturated monoglycerides without water and with water system. The mixed saturated and unsaturated monoglycerides in water show a sub-α phase, two types of α-gel phase, L_α, L_2, β_1 and three bicontinuous cubic phases, Ia3d, Pn3m and Im3m. On further heating, all cubic phase types convert to a hexagonal phase.

The nomenclature of the phases in these systems is very complicated [25]. We have employed the nomenclature shown in Table 1.

2. Experimental

2.1. Materials, sample preparation

Glycerol monooleate (GMO) and glycerol monostearate (GMS) were obtained from Givaudan. The GMO and GMS formulations contain greater than 90% monoglycerides and less than 10% diglyceride and triglyceride [24]. A mixture of monoglycerides G50 containing 50% of GMS and 50% of GMO was heated to 80 °C and held constant for 30 min using a hot plate with magnetic stirrer. Ten different samples of the surfactant mixture with varying water content were examined. Some main abbreviations are listed in Table 2. We label the samples by the percentage water content, i.e. W12.5 corresponds to a sample with 12.5% water, and 87.5% of the surfactant mixture.

2.2. Temperature controlled optical microscopy

The systems were observed using a Carl Zeiss Axioplan-2 polarising optical microscope. Photographs were taken using a JVC-TK 1280E CCD camera and analysed via Linkam software. The temperature of the sample was controlled by the Linkam hot-stage (±0.5 °C) attached to the optical microscope. A stream of nitrogen gas from a reservoir of liquid nitrogen was used to control cooling rates, and heating and cooling rates were fixed at 5 ± 0.2 °C/min. Phase penetration scans can be used to obtain the general liquid crystal phase behaviour as a function of concentration and temperature [26]. A small amount of surfactant is placed on the microscope slide below a cover slip. Water is then introduced at the edge of the cover slip by a pipette. Water is brought into contact with the edge of the surfactant creating a concentration gradient by capillary forces. Mesophases may form at the solute/solvent interface and appear

Table 2
Composition (% (w/w)) of samples examined.

Monoglycerides	Sample label	Composition of water % (w/w)
50% GMS/50% GMO (G50)	W12.5	87.5% G50 + 12.5% water
	W25	75% G50 + 25% water
	W50	50% G50 + 50% water
	W75	25%G50 + 75% water