

State diagrams for binary monoglyceride mixtures

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INTRODUCTION & AIM

Oleogels are colloidal systems in which an organic solvent is entrapped within a supramolecular network. Structured with edible vegetable oils (VO), they can replace solid fats in foods, while those with mineral oils (MO) serve cosmetic applications. Monoglycerides (MG) act as low-molecular-weight gelators, self-assembling during cooling into an inverse lamellar phase ( $L\alpha$ ), then sub- $\alpha_1$  and sub- $\alpha_2$  phases, before slowly forming the thermodynamically stable  $\beta$  phase, which can cause crystal agglomeration and oil syneresis. MG transitions are influenced by composition, concentration, and oil type, affecting crystal morphology, oil-binding, and rheological properties. This study examined structural transitions and rheological evolution of 8% binary MG mixtures (C14, C16, C18, C22) in VO and MO, with emphasis on eutectic mixtures that form common crystalline structures with enhanced mechanical properties for food and cosmetic applications.

METHOD

**DIFFERENTIAL SCANNING CALORIMETRY:** The thermal behavior of pure MGs (>99%) and 8% (w/w) MG binary mixtures in VO or MO was analyzed using a DSC (Q2000, TA Instruments) with T-zero pans. Samples were heated to 80 °C for 20 min, cooled to −20 °C at 10 °C min<sup>−1</sup>, held for 2 min, and reheated to 80 °C at 5 °C min<sup>−1</sup>. From the cooling and heating thermograms,  $T_{crj}$ ,  $\Delta H_{crj}$ ,  $T_m$ , and  $\Delta H_m$  were determined. Phase diagrams for the 8% MG mixtures with C18 were constructed by plotting the mole fraction of each MG (C14, C16, or C22) against the  $T_m$  of the corresponding polymorphic transition ( $L\alpha$ , sub- $\alpha_1$ , or sub- $\alpha_2$ ) (Fig 1).

**RHEOLGY:** Rheological properties of 8% (w/w) MG binary solutions in VO or MO were measured using a Discovery HR-3 rheometer with a steel plate–plate geometry. Samples were loaded and subjected to the same thermal protocol used in the DSC analysis. The elastic ( $G'$ ) and viscous ( $G''$ ) moduli were recorded during cooling and the isothermal stage within the linear viscoelastic region. Two replicates were performed, and mean  $G'$  values were plotted as a function of temperature and time (Fig 2).

RESULTS & DISCUSSION

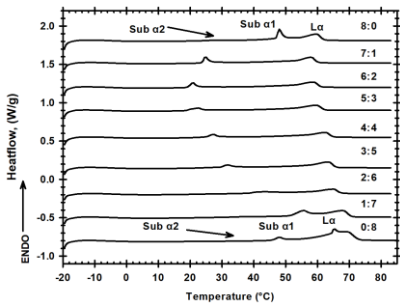


Fig 1. Heating thermogram at different proportions of C18:C16 in VO.

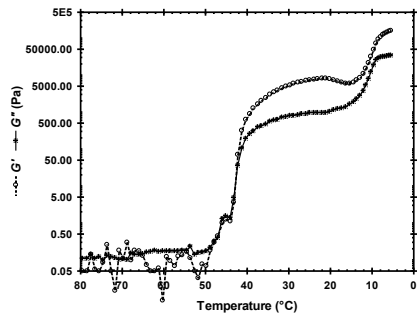


Fig 2. Evolution of the elastic modulus ( $G'$ ) during cooling for C18:C16 mixture in VO at the eutectic proportion (0.356 molar fraction of C18).

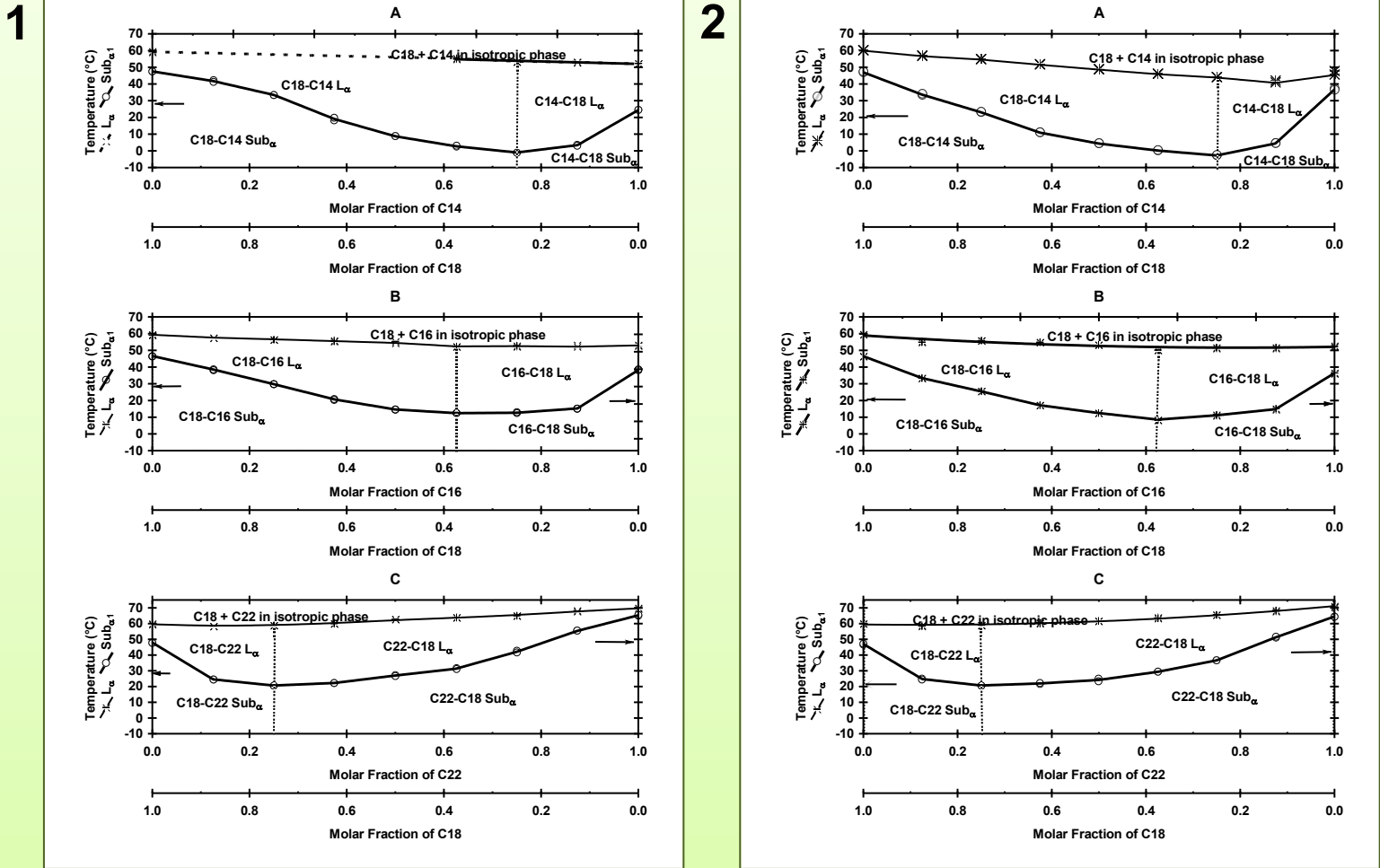


Fig 3. State diagrams for the MG binary mixtures in vegetable oil (1) and mineral oil (2). The dotted line indicates the molar fraction composition of the mixed MG crystal at the eutectic point. Letters A, B and C indicate components in MG binary mixtures (C18:C14, C18:C16 and C18:C22 respectively).

Figure 3 shows that the eutectic behavior for the formation of the lamellar  $L\alpha$  phase and the sub- $\alpha_1$  polymorph that was observed only in the C18:C14 mixture, with the strongest effect seen in the sub- $\alpha_1$  transition. In the C18:C16 and C18:C22 mixtures,  $L\alpha$  formation occurred over narrow temperature ranges from 50 to 60 °C for C18:C16 and from 60 to 70 °C for C18:C22. For C18:C16, the  $L\alpha$  melting temperature increased with higher C18 content, while for C18:C22 it decreased. Similar phase behavior was observed in both vegetable and mineral oils, indicating limited influence of oil type on monoglyceride transitions. The sub- $\alpha_1$  eutectic temperature shifted to higher C18 fractions as the alkyl chain of the other MG increased from C14 to C22. The sub- $\alpha_2$  polymorph appeared only in pure C16, C18 and C22, and was absent in all binary mixtures (Table 1).

Overall, the elasticity ( $G'$ ) of organogels formed with the monoglyceride mixtures after 180 min at 5 °C was higher in vegetable oil than in mineral oil, especially for the C18:C14 mixture at a molar fraction of 0.125. The enhanced elasticity of the C14:C18 mixture was linked to the formation of the  $\beta$  polymorph during storage at 5 °C. In contrast, the  $\beta$  polymorph did not develop in the C18: C16 or C18: C22 systems under the same storage conditions.

CONCLUSION

This study reports eutectic behavior of sub- $\alpha$  phases in binary MG mixtures, enhancing oleogel elasticity by promoting inefficient chain packing and oil retention. Vegetable oil oleogels were more elastic than mineral oil. Sub- $\alpha$  phases are metastable, eventually forming  $\beta$  phases, highlighting the need for gelator strategies to stabilize oleogels for food and cosmetics.

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