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ORIGINAL PAPER

The Effect of Partial Acylglycerols on the Exchange Between Liquid and Solid Tripalmitoylglycerol

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Abstract Exchange of molecules between liquid and solid components of a triacylglycerol (TAG) system is an important process in the degradation of many food components as well as for many industrial processes such as fractionation. NMR is a technique that can be used to measure the exchange between solid and liquid phases. In this work we show that monoacylglycerols (MAG) and diacylglycerols (DAG) have a retarding effect on the rate of exchange between solid and liquid TAG. In particular dipalmitoylglycerol significantly retards the rate of exchange. It is postulated that this result suggests that exchange occurs primarily through certain hotspots, probably kinks and defects on the crystal surface. MAG and, in particular, DAG can block these hotspots. It is suggested that because of their molecular structure they can partially co-crystallize with the TAG crystal during the exchange process and then block further exchange.

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Introduction

Many different phenomena in the area of lipids depend upon the interaction between liquid and solid fats. Areas include the development of bloom in chocolate and the behaviour of fats during fractionation processing. The general aging of semi-solid products is also dependent upon the exchange between liquid and solid components. If we could reduce the exchange rate between the different components then the rate of change (deterioration) of the system as a whole could be reduced, or some other process could be optimised. In fractionation, a slower exchange between different fats could lead to a better separation and in chocolate to less bloom.

In order to be able to do this, the nature of the interaction between liquid and solid triacylglycerol (TAG) must be understood. This is problematic because the species are similar and overall transformation may be negligible or indeed zero for a system at or close to equilibrium. Nevertheless, in previous work, we investigated the interaction between solid and liquid tripalmitoylglycerol (PPP) [1–3] either by radio labelling or by an NMR labelling method. In both types of experiments, chemically identical but isotopically distinct PPP molecules were followed as they were transferred between solid and liquid phases. By these means, we have been able to measure the rates of exchange between liquid and solid PPP systems at equilibrium. In particular, we found that for a saturated solution of PPP crystals in Medium-Chain TAG (MCT) oil at 40 °C, there was an exchange corresponding to about three layers of

molecules per hour (assuming uniform exchange over the crystals). However, we could not preclude that the exchange occurs primarily at certain more energetic sites and that this exchange on the molecular level was part of an Ostwald-type ripening process, even though this was thought to be unlikely.

In real systems, emulsifiers and other additives can be added in an effort to retard interaction and unwanted transformation. Options that are used include the use of behenic acid to retard the formation of chocolate bloom [4] and the use of monoacylglycerols (MAG) and their derivatives to prevent recrystallisation in margarine [5]. These products could conceivably function by suppressing molecular exchange. However, this and its mechanism are not yet clear. It is the objective of this work to identify if partial acylglycerols affect the interaction between the solid and liquid phases of a TAG system.

The effect of impurities on the crystallization of TAG systems has been of scientific interest over many years. Of particular relevance to this work is the effect of diacylglycerol (DAG) on TAG crystallization. Retardation on growth of pure trilaurin has been found [6] and the importance of chain length matching between DAG and TAG for a large effect shown [7]. Other research has shown the effect of DAG in more complex systems, such as cocoa butter [8, 9]. Also similar results have been seen on cocoa butter equivalents (CBEs) [10]. It has also been shown [11] that DAG encourages the β polymorph of TAG.

Experimental

Materials

PPP and the partial acylglycerols were purchased from Sigma Chemicals. MCT oil was a gift from Karlshamns AB, Karlshamn, Sweden.

The surface area of the PPP crystals was determined as 2.077 m^2/g from krypton gas adsorption measurements using Brunauer, Emmett and Teller (BET) isotherms.

Methods

Saturated solutions of ^{2}H-labelled PPP in medium chain triacylglycerol (MCT) oil were prepared as described previously [3]. To the solution so made, 0–5% of partial acylglycerol (measured as a weight fraction of the PPP in solution) was added. The solution was equilibrated at 40 °C and 1.50 ml were added to 50 mg of characterised PPP crystals and then vigorously stirred for a few seconds. The resulting blend was immediately transferred to an NMR machine (Bruker AMX 300) at 40 °C and the experimental readings by ^{2}H NMR were begun. Experimentation was performed in the same way as in [3]. After commencement of a run, ^{2}H spectra were recorded at regular intervals. The signal was typically obtained by averaging 64 scans with a small recycling delay. In brief, under the set acquisition conditions, any ^{2}H-labelled PPP that is in the crystal remains undetected. In particular, discrete measurement points were taken every 6 min and experiments were typically, with the exception of a few longer runs, allowed to run for between 1 and 1.25 h. During an experimental run there was a continuous exchange between the labelled PPP in solution and the unlabelled PPP in the added crystals. Therefore, there was a decrease in the total amount of labelled PPP in the liquid phase, which was manifested as a decrease of the ^{2}H NMR signal intensity Hence, by measuring the rate of decrease of ^{2}H NMR signal we obtained an estimate of the overall rate of exchange.

Results

The results for increasing concentration of monopalmitoylglycerol (MP) from 1 to 5% are shown in Fig. 1. The graph shows the proportion of labelled PPP in the liquid at any one time. Clearly, the reduction in the exchange rate was roughly proportional to the amount of MP added; 5% MP reduced the exchange by about 20%. As shown in Fig. 2, there was a difference in the effect of the different MAG, such as MP and monooleoylglycerol (MO).

The effects of DAG on the exchange are shown in Fig. 3. Of particular notability is the effect of dipalmitoylglycerol (DP). This decreased the exchange rate by around 70%, bringing exchange to a virtual standstill.

Measurements were performed in at least triplicate. The variation in rate was of the same order as that reported previously [3]. Variation of up to ±5% was observed.

Discussions

It seems that the presence of partial acylglycerols in our system interfered with the exchange process and decreased the exchange rate. Since the exchange occurred at the crystal–liquid interface, the interference step must also have occurred at this interface. The second important observation is that exchange was inhibited already at relatively low concentrations of added partial acylglycerols. It cannot be expected that this low amount would interfere with processes occurring across the entire surface area. If we assume full surface coverage for the DP then we would have a surface layer corresponding to approximately

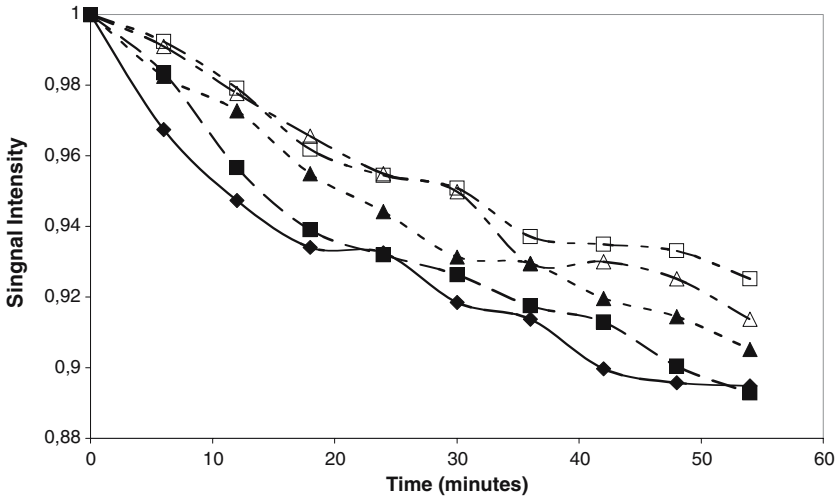

Fig. 1 Effect of increasing concentration of monopalmitoylglycerol on the exchange of tripalmitoylglycerol over 1 h (*filled diamond*s 0%, *filled square*s 1%, *filled triangle*s 2%, *open triangle*s 4% and *open square*s 5%)

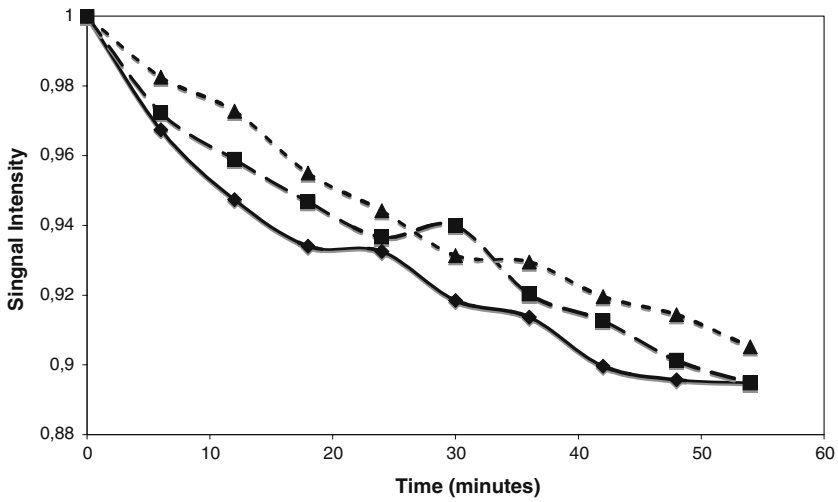

Fig. 2 Effect of 1% monoacylglcyerol on the exchange of tripalmitoylglycerol over 1 h (*filled diamond*s 0% monoacylglcyerol, *filled square*s 1% monopalmitoylglycerol and *filled triangle*s 1% mono-oleoylglycerol)

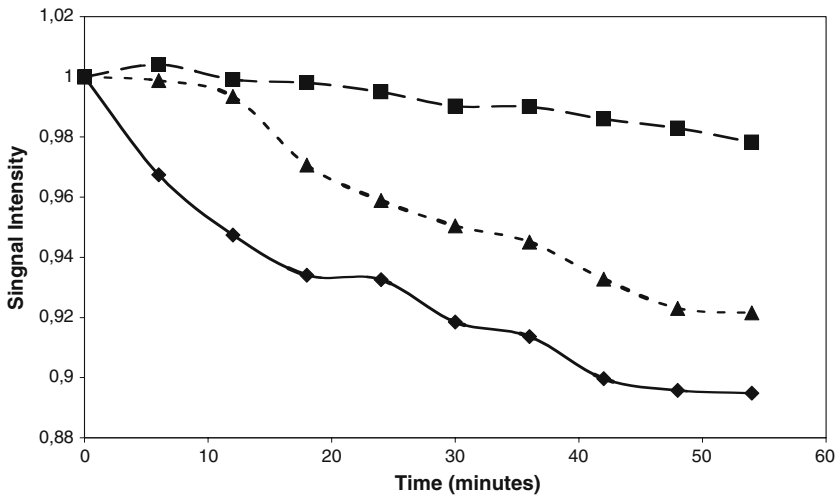

Fig. 3 Effect of 1% diacylglycerol on the exchange of tripalmitoylglycerol over 1 h (*filled diamond*s 0% diacylglcyerol, *filled square*s 1% dipalmitoylglycerol, and *filled triangle*s 1% dioleoylglycerol)

2×10^{-3} g/m^2. A full surface monolayer of closely packed DP molecules is several orders of magnitude lower than this. Therefore it is conceivable, if unlikely that the entire surface could be covered by DP molecules. However, it is extremely unlikely that a uniform monolayer could cover the surfaces of the crystals so quickly.

Therefore we postulate that most exchange is occurring at specific surface hotspots; these could be specific planes or regions where there is a highly defected surface structure. It seems that the partial acylglycerols can poison these sites. The observed high molecular specificity of the inhibition effect supports this idea; blocking exchange by simply adsorbing on the full crystal surface and thereby reducing crystal–liquid contact would require very different adsorption isotherms for the different partial acylglycerols.

Analogous behaviour has been reported for the effect of partial acylglycerols on the crystallisation of TAG [6, 7]. These authors postulated that the effect of the different partial acylglycerols occurred because of specific interactions between the acylglycerols and the crystallising TAG. They suggested that those molecules can co-crystallise and, in particular, the chains of partial acylglycerols can be incorporated into the growing TAG crystals. However, the head group will leave a defect at the surface, which may be a hindrance to growth so that the next molecules are not able to join onto the surface. Hence, growth at that site can be dramatically slowed down. The effect was shown to be extremely molecular sensitive, with DAG having the largest effect.

This behaviour suggests a mechanism for our system with the following elements. First, we must partly revise our previous findings [3]: if the molecular exchange between solid and dissolved PPP is sensitive to crystallization-related phenomena, it involves crystal growth and, by having a constant amount of crystals, crystal dissolution. This indicates a ripening process. Hence, our observed exchange can be blocked in two ways: either on the growth side or on the dissolution side. To be in line with the crystallization behaviour, we suggest that (i) growth occurs primarily at specific hotspots, (ii) a partial acylglycerol attaches to one of those regions and co-crystallizes with its acyl side-chain(s) towards the crystal, where (iii) the defective head group hinders further growth by setting a high steric penalty for being surrounded by TAG (Fig. 4). Thus, growth hotspots are poisoned and the total rate of crystal growth decreases. Since the liquid is PPP-saturated, dissolution must also slow down together with the overall rate of exchange.

Note that our measurement times are of the order of minutes, whereas molecular timeframes are much faster. Hence, all molecules can access all crystal faces and any observed differences between different partial acylglycerols are not kinetically related. Since DP crystal structure is similar to that of the PPP, the particularly large inhibition by the former may be a consequence of high concentration of DP involvement at the PP crystal faces. From crystal growth considerations we can postulate that growth occurs primarily at ledge sites. Further work, possibly X-ray diffraction, would be necessary to prove this.

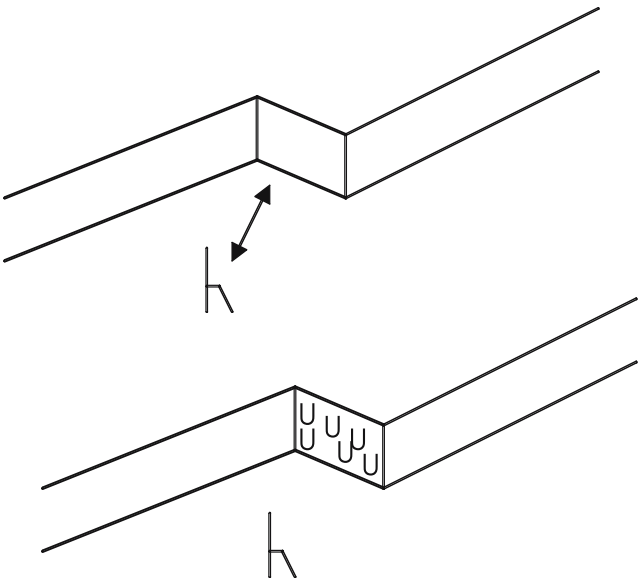

Fig. 4 Postulated effect of monopalmitoylglycerol on the blocking of exchange sites for liquid and solid tripalmitoylglycerol, **a** no dipalmitoylglycerol, **b** dipalmitoylglycerol adsorbing and blocking exchange at an exchange site

The MCT oil that is used in the experiments has a certain proportion of DAG (3.2%). Thus there can be expected to be a certain effect of this DAG on the results from the previous work [2], and on the experiments reported here. However, the DAG molecules in this case will consist of the fatty acids that already exist in the TAG in the MCT oil. Thus they will be primarily caprylic (8:0, 61.8%) and capric acid (10:0, 37.6%). These are significantly shorter than the palmitic acid chains in the recrystallizing molecules. The effect of molecules with significantly different chain-lengths on the recrystallizing species is thought to be limited. This has been shown for crystallizing TAG [7] and is thought to be likely here. Therefore it is the addition of the palmitic acid containing molecule in this case that shows a significant effect.

In a triacylglycerol crystal, the TAG molecules will primarily interact via van der Waals forces between acyl chains. As a consequence, the addition of a partial acylglycerol molecule to a crystal is relatively easy and they can bind easily into the crystal lattice. We can postulate the differences between the behaviour of MAG and DAG molecules in the crystal. DAG molecules are larger and more like TAG than MAG because of the extra chain. Therefore they would be expected to bind more strongly into the crystal lattice. Thus, for an equivalent concentration of molecules we can expect there to be a higher concentration of additive molecules and a longer residence time in the crystal for a system with DAG than MAG.

MAG molecules are more different than DAG from TAG. Thus MAG molecules at a crystal interface are likely to poison growth more effectively than DAG ones. The next TAG molecule joining the system will be joining at a spot with only one acyl chain rather than two, inhibiting growth more effectively. Therefore the overall effects of MAG and DAG molecules in a system will depend upon a balance of their residence time (favoring DAG) and their effectiveness as a growth poisoner (favoring MAG). In this particular case it seems that the increased residence time of the DAG is more significant than the enhanced poisoning ability of the MAG.

This study described recrystallization in near equilibrium conditions. In more applied situations, other factors will come into play in determining behavior. In particular the role of different TAG in the system and their interplay and mutual interaction is important, as is the effect of temperature fluctuations and chemical composition variation in the system. These points need to be considered in further investigations. In order to fully understand the basis for the recrystallization behavior of TAG, a model must be developed that will allow for all such factors to be included.

Conclusions

We find that MAG and DAG inhibit molecular exchange between solid and dissolved PPP. This inhibition is highly molecule-specific and is thereby explained in terms growth inhibition at hot-spots on particular crystal faces. This result suggests that diglycerides could be particularly good additives for inclusion in a food product with the aim of preventing exchange and subsequent transformation. Of course they may have other deleterious effects on a product and so alternatives need to be considered. Derivatives of the diglycerides could be better in that respect and could even prove to be more effective as recrystallization inhibitors.

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