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# Investigation of phase transitions in pure and gas-saturated triglycerides up to 20 MPa by thermal analysis according to Smit

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## Abstract

The phase behaviour of the saturated monoacid triglycerides tripalmitin, tristearin and triarachidin has been studied for the pure compounds at normal pressure as well as under the influence of dissolved helium, nitrogen and argon at pressures up to 20 MPa with thermal analysis according to Smit.

Under the experimental conditions applied two phase transitions are observed during the linear heating process for all triglycerides and all gases: transition from the metastable  $\alpha$ -phase into the thermodynamically stable  $\beta$ -modification and the melting of the  $\beta$ -modification. Within the pressure and temperature range which has been examined the T(p) phase boundaries form essentially straight lines with slopes depending on the dissolved gas. Generally the slopes decrease when changing from helium to nitrogen and from nitrogen to argon.

From the difference between the transition temperatures under helium and nitrogen as well as under helium and argon at a given pressure the mole fractions of dissolved nitrogen and argon are estimated as a function of pressure.

*Keywords:* Gas solubility; High pressure; Polymorphism; Thermal analysis (Smit); Triglycerides

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## 1. Introduction

Polymorphism of saturated even monoacid triglycerides has been studied by different authors with different experimental techniques such as X-ray diffraction [1–5],

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DTA [6–7] and DSC [8–9]. The scheme of possible phase transitions is rather complex. Most transitions are monotropic and furthermore the occurrence of unstable liquids during the transitions is postulated [10]. Although the phase behaviour of triglycerides is well known now under normal pressure, to the best of our knowledge no investigations have so far been performed under high pressure.

DTA measurements in our laboratory on pure and gas-saturated liquid crystals have shown that the properties and the structure of mesomorphic phases are influenced by the saturating gases used in a quite individual and characteristic manner [11]. In continuation of this work, the phase transitions of the triglycerides tripalmitin (PPP), tristearin (SSS) and triarachidin (AAA) have been studied by thermal analysis according to Smit [12–14] under the influence of helium, nitrogen and argon in order to provide further information about the nature of these transitions and the solubilities of these gases in the triglycerides. Such investigations are also of interest for the understanding of transport phenomena in cell membranes.

## 2. Experimental

The triglycerides under test were purchased from Sigma and used without further purification (purity approximately 99%).

The measurements were carried out in a Smit apparatus according to the thin film method [12,13]. The cylindrical measuring vessel had been modified for investigations under pressures up to 20 MPa. It is made of a Cu–Be alloy. A platinum resistance thermometer (inner thermometer) is centred in the vessel and surrounded by a cylindrical steel jacket in order to protect it against the gas pressure. The inner diameter of the measuring vessel is 5.6 mm, the outer diameter of the steel jacket is 5.0 mm. The vessel is filled by melting 700–800 mg substance and then screwed up. Thus the substance forms a thin film of about 0.3 mm thickness in the remaining space. The measuring cell can be connected to a gas supply. The pressure-transmitting gas acts directly on the sample under test.

The calorimeter consists of a cylindrical block of brass containing a coaxial air space where the measuring vessel is mounted. The block is surrounded by a heating wire. A constant heat supply is achieved according to the method of Thomas and Parks [15] by using a second platinum resistance thermometer (outer thermometer), which is inserted into the calorimeter block. Both resistance thermometers are part of a Wheatstone bridge in the heating controller, which sustains constant resistance and consequently temperature differences between inner and outer thermometer.

During the measurements the whole calorimeter block is inserted into a dewar flask. The heating rates used are between 0.15 and 0.2 K min<sup>-1</sup>. The resistance of the inner thermometer is recorded as a function of time by a computer in 15 s intervals. The corresponding temperature is calculated from a calibration function, which was determined by calibration against a platinum resistance temperature detector in an oil bath. The calibration of this detector according to the International Practical Temperature Scale of 1968 (IPTS -68) is traceable to NIST.

### 3. Results and discussion

Depending on the cooling rate of the melt the triglycerides under test crystallize either in the  $\alpha$ - or  $\beta$ -modifications. Slow cooling provides the thermodynamically stable  $\beta$ -modification, and the heating curve shows only one transition from the  $\beta$ -phase to the melt ( $\beta \rightarrow l$ ). After rapid cooling the triglycerides crystallize in the metastable  $\alpha$ -modification. Then two transitions are observed in the heating curve: the transition from the  $\alpha$ -phase to the  $\beta$ -modification and the melting of the  $\beta$ -modification ( $\alpha \rightarrow \beta \rightarrow l$ ). All measurements in this work have been carried out after rapid cooling in order to observe both transitions.

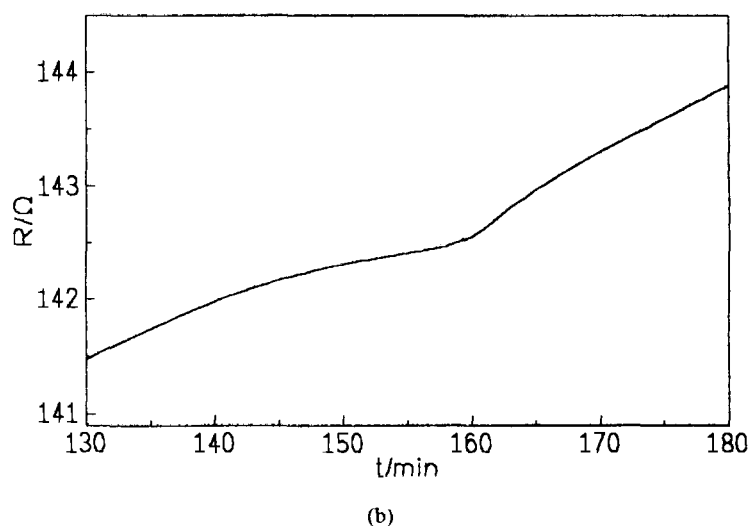
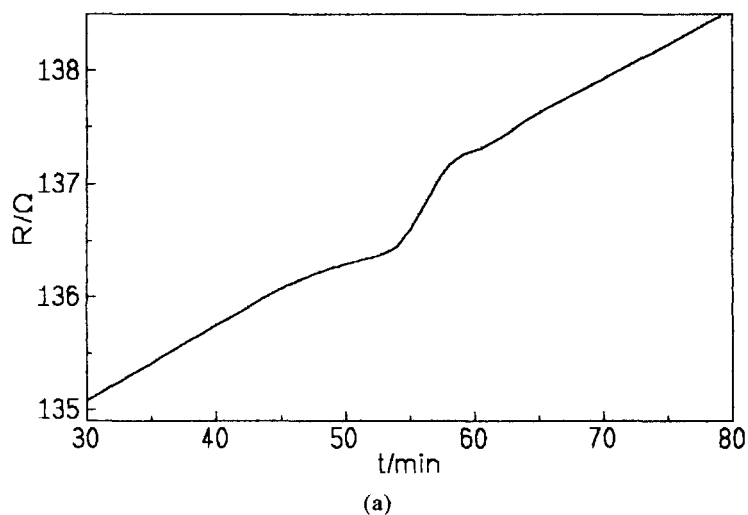


Fig. 1. Heating curve of AAA: (a)  $\alpha \rightarrow \beta$  transition; (b)  $\beta \rightarrow l$  transition. For experimental details see text.

Fig. 1 shows an original  $R(t)$  curve (resistance against time) for AAA under normal pressure. The  $R(t)$  curve of the  $\alpha \rightarrow \beta$  transformation (Fig. 1a) indicates a change from an endothermic to an exothermic process of transition; at first the heating curve flattens, then it shows a sudden rise, before it returns to linearity. This corresponds to observations made by Mathieu et al. [6] during DTA measurements with SSS and can be explained as follows. The  $\alpha$  modification melts endothermically providing an unstable  $\alpha$  melt which then exothermically crystallizes in the stable  $\beta$  modification. For this process the transition temperature has been defined here as the first deviation from linearity of the heating curve. Fig. 1b shows the  $R(t)$  curve of the endothermic transition  $\beta \rightarrow l$ .

The  $T(p)$  phase boundaries of the observed transitions in the gas-saturated triglycerides are shown in Fig. 2. They are nearly straight lines with slopes depending on the nature of the pressure-transmitting gas.

- (1) Under helium an increase of the transition temperature is found for the  $\alpha \rightarrow \beta$  transition as well as for the  $\beta \rightarrow l$  transition with rising pressure that is linear within the limits of experimental error.
- (2) For nitrogen the same effect is observed, but in this case the slopes of the phase boundaries are less positive.
- (3) Under argon the melting temperature for the  $\beta \rightarrow l$  transition remains nearly constant up to 20 MPa, whereas for the  $\alpha \rightarrow \beta$  transition a decrease in the transition temperature is observed with rising pressure that is linear within the limits of experimental error.

The influence of the different gases on the transition temperatures can qualitatively be explained taking into account two competing pressure effects [11]:

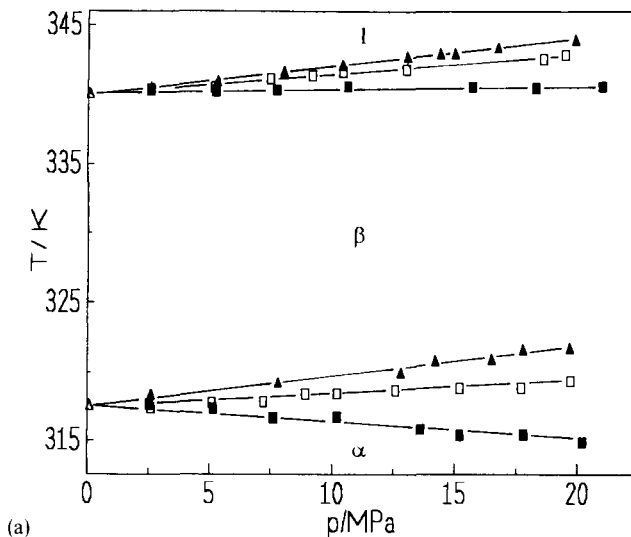


Fig. 2. Phase behaviour of PPP (a), SSS (b) and AAA (c) saturated with He  $\blacktriangle$ , N<sub>2</sub>  $\square$  and Ar  $\blacksquare$  ( $\triangle$ : normal pressure).

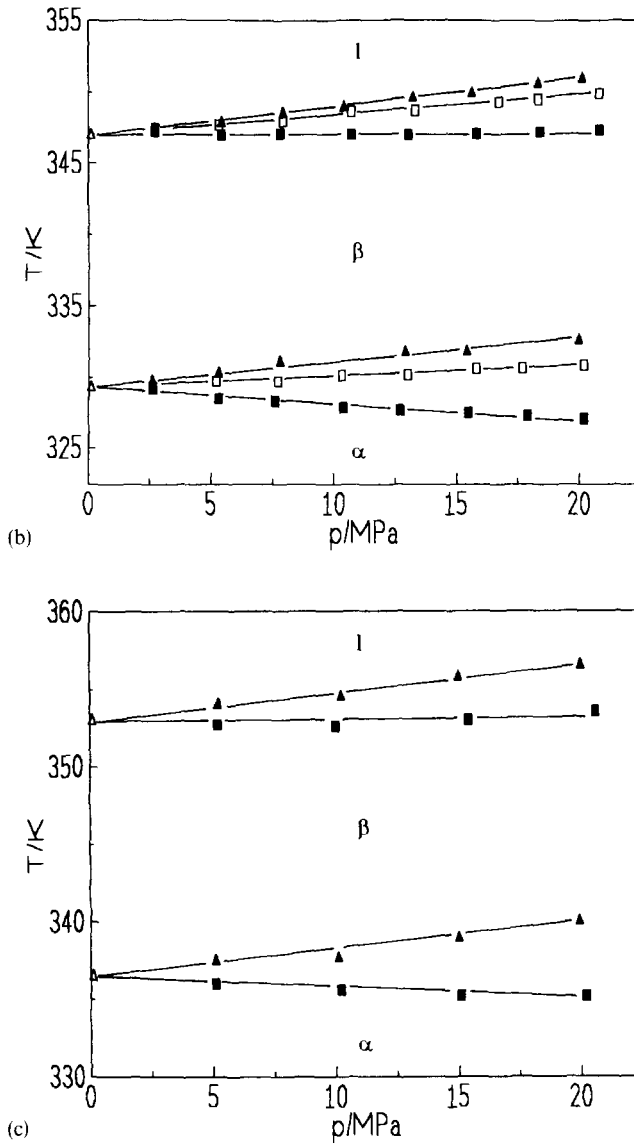


Fig. 2. (Continued)

- (1) The transition temperature increases with rising pressure.
- (2) The solubility of the gas in the melt increases with rising pressure. The dissolving gas can be regarded as an inert impurity which causes a depression of the transition temperature.

For helium, effect (1) dominates as it is only slightly soluble in liquids. For nitrogen, effect (1) is still prevailing while effect (2) is getting more important.

Under argon there is a compensation of the effects (1) and (2) for the transition  $\beta \rightarrow l$  in the examined pressure range so that the transition temperature is practically independent of the pressure. For the transition  $\alpha \rightarrow \beta$  effect (2) dominates thus confirming the occurrence of an intermediate melt during the transformation.

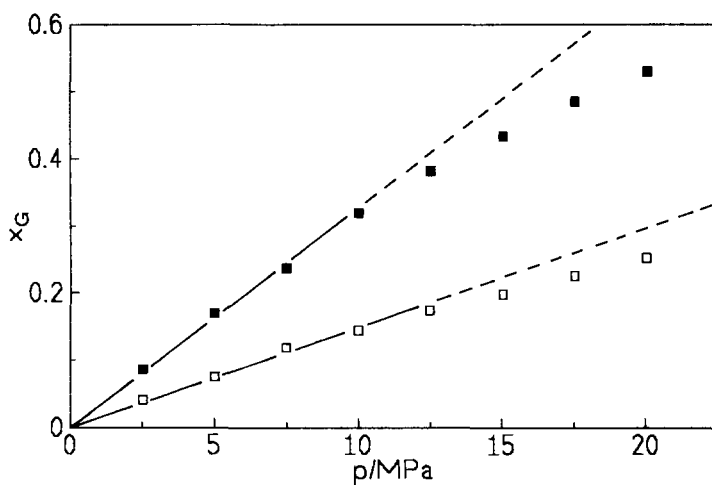
The observed influence of the gases on the phase transitions in triglycerides confirms the results obtained by Krombach and Schneider in DTA measurements with gas-saturated liquid crystals: The solubility of the gases in the melt increases from helium to nitrogen and from nitrogen to argon [11].

The weak increase of the melting temperature for the  $\beta \rightarrow l$  transition under nitrogen and argon compared to helium suggests an increase of the mole fraction of nitrogen or argon dissolved in the melt with increasing pressure. However, the determination of impurity from the melting curve according to the Smit method fails to give an increasing mole fraction of impurity with increasing pressure. Here the assumptions of the Smit method are invalid because of the high solubility of nitrogen and argon in the melt; it can only be applied for mole fractions of impurity smaller than 0.02 [12]. So a different approach for the estimation of the mole fraction of gas dissolved in the melt is tested. As a first approximation we can treat the gas-saturated triglyceride as an ideal binary system with complete miscibility in the liquid phase and complete immiscibility in the solid phase. It has already been shown that the influence of dissolved helium on phase boundaries is comparatively small even for pressures up to 250 MPa [11]. So the assumption seems to be justified that the transition temperatures of pure and helium-saturated triglycerides at a given pressure are equal in the pressure range examined ( $T_{\text{trs}}^*(p) = T_{\text{trs}}^{\text{He}}(p)$ ). Then we can write for the mole fraction  $x_l$  of the triglyceride and for the mole fraction  $x_G$  of nitrogen or argon in the melt:

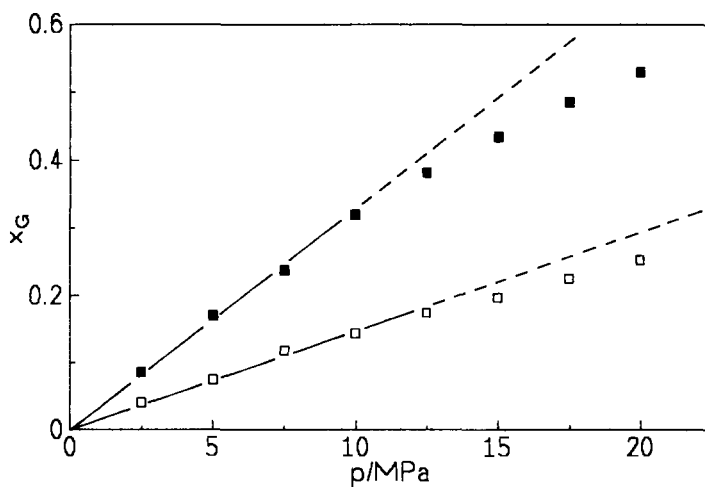
$$x_l = 1 - x_G \approx \exp \left[ -\frac{\Delta_{\text{fus}} H_m^*}{R} \left( \frac{1}{T_{\text{trs}}^G(p)} - \frac{1}{T_{\text{trs}}^{\text{He}}(p)} \right) \right] \quad (1)$$

where  $\Delta_{\text{fus}} H_m^*$  is the enthalpy of fusion of the pure triglyceride, which is assumed to be independent of the pressure;  $T_{\text{trs}}^{\text{He}}$  and  $T_{\text{trs}}^G$  are the transition temperatures of the helium-saturated, nitrogen-saturated or argon-saturated triglycerides, respectively.

The transition temperatures at a given pressure can be determined from the phase diagrams by linear interpolation. Fig. 3 shows the mole fractions of nitrogen and argon in the melt calculated with Eq. (1) for both transitions in SSS. For PPP and AAA analogous results are obtained. For pressures up to 10 MPa there is a linear increase of the mole fraction of dissolved gas with increasing pressure. At higher pressures the curve bends off. This might indicate a decreasing dependence of the concentration of saturation on the pressure. However, this bending off may also result from the neglect of activity coefficients in Eq. (1). For argon the calculated mole fraction is about 0.5 at 20 MPa. This seems to be very high, but can be explained by the great difference between the molar masses of the triglycerides ( $M_{\text{SSS}} = 891.5 \text{ g mol}^{-1}$ ) and argon ( $M_{\text{Ar}} = 39.9 \text{ g mol}^{-1}$ ): A mole fraction of argon of 0.5 corresponds to a mass fraction of only 0.043; thus the calculated mole fractions seem to be quite reasonable. Add to this



(a)



(b)

Fig. 3. Mole fraction of  $x_G$  of N<sub>2</sub>  $\square$  and Ar  $\blacksquare$  dissolved in the melt of SSS for the  $\alpha \rightarrow \beta$  transition (a) and  $\beta \rightarrow l$  transition (b) as a function of pressure.

that the present solubility data correspond quite well with normal pressure results on the solubilities of nitrogen, argon and other gases in olive oil obtained by Battino et al. [16].

The investigations are continuing, with the special aim of obtaining more quantitative information about the polymorphism of complex substances, such as selected glycerides and their mixtures, as well as about the influence of dissolved gases on phase stability.

## Acknowledgements

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