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# The sound velocity measurement in diacylglycerol oil under high pressure[†]

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In this article, the influence of high pressure on sound velocity at 293 K has been presented. The investigated diacylglycerol oil (DAG – [D82T18]AG) was composed of 82% DAGs and 18% triacylglycerols. The variation of sound velocity with hydrostatic pressure for DAG was evaluated up to 400 MPa. The phase transformation in DAG has been observed as a discontinuity of the dependence of sound velocity on pressure. The sound velocity during the phase transition has shown distinct increment. Also the volume changes have been measured. It has shown the rapid drop of the volume at the phase transformation pressure due to the possible crystallization of DAG oil.

**Keywords:** high pressure; velocity; DAG

## 1.   Introduction

Research on the high pressure properties of a wide class of lipid compounds have been stimulated by the development of industrial methods of high pressure food conservation. A special attention was paid to the pressure-induced changes of edible oils since the phase transitions were observed during these processes [1–8]. Naturals oils such as castor oil [1], rapeseed oil [2], soy oil [3] and others [5–8] and their main components *i.e.* triacylglycerols (TAGs) [6,9,10] are intensively studied. Later, the research was extended to fatty acids [11–15] and lately on diacylglycerols (DAGs) [16,17]. In the meantime, the range of experimental methods was extended from basic optical measurements [9,10,12,16] to dielectric properties [13] and on ultrasonic methods of measuring viscosity [17,18] and sound velocity [19,20]. In this article, the results of sound velocity measurement during DAG oil compression has been presented.

DAGs are esters of the trihydric alcohol glycerol in which two of the hydroxyl groups are esterified with fatty acids. They consist of two fatty acid chains bond to a glycerol molecule.

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Table 1. Main components of the investigated DAG oil sample.

| Fatty acid carbon atoms: C=C bonds | Amounts (%) |
| --- | --- |
| C14:0 | 0.1 |
| C16:0 | 4.5 |
| C16:1($\Sigma$) | 0.5 |
| C17:0 | 0.1 |
| C17:1 | 0.1 |
| C18:0 | 2.5 |
| C18:1($\Sigma$c) | 59.1 |
| C18:2(cc) | 19.6 |
| C18:3(ccc) | 8.9 |
| C20:0 | 1.9 |
| C20:1($\Sigma$) | 1.0 |
| C22:0 | 0.1 |
| C22:1($\sigma$) | 1.2 |
| C24:0 | 0.3 |
| C24:1 | 0.1 |

Since two fatty acid chains can bond to two of the three possible positions, there are three isomers of DAGs named sn-1,2, sn-2,3 and sn-1,3. The isomer sn-1,3 has one additional plane of symmetry, therefore, it has different thermodynamic properties from the other two (for instance higher melting temperature, higher viscosity coefficient). Main components of the investigated sample DAG oil are given in Table 1. Similarly to other lipids, DAG can crystallize into several polymorphic forms [21,22]. In case of natural DAGs, two acyl chains may consist of two different fatty acids of different chain length (the so-called mixed chain DAGs). The most stable crystalline phase is the so-called beta phase, a monoclinic crystalline form with an orthorhombic perpendicular sub-cell chain packing, in which both acyl chains are parallel to each other. The molecules are organized into a bi-layer structure, with the glycerol backbone roughly parallel to the plane of it, and the acyl chains tilted at approximately 60 degrees with respect to that plane. The acyl chain unsaturation, and particularly a single *cis* unsaturation, impairs chain packing. The diversity of the mixed chain DAG results in an increased number of metastable crystalline phases.

Monoacylglycerols and DAGs are common food additives used to blend together certain ingredients, such as oil and water, which would not otherwise blend well. Partially hydrogenated soya bean and canola oil are the main sources of glycerols. They may also be synthetically produced. Edible oils consisting of about 80% of 1,3-DAGs are sold in Japan as nutritional supplements. It is claimed that they are metabolized in a different way than the DAGs are, and with a beneficial nutritional effect [23–26]. The 1(3)-monoacylglycerols when digested are rather poorly absorbed, apparently limiting the accumulation of fats in body tissues.

When fatty materials are used as food products, knowledge of their physical properties is of great importance, especially with regard to interfacial tension, solubility, viscosity, melting behaviour and other physicochemical characteristics of the material. DAG oil produced for direct consumption was investigated in our first experiments.

## 2. Experimental setup

High pressure measurements were performed using a set-up that was designed and made at Warsaw University of Technology. Pressure was applied by a manually driven hydraulic press [8,27]. Pressure and temperature sensors were located inside the 22 cm$^3$ pressure chamber within the investigated DAG oil sample. The pressure was measured by a manganin sensor, calibrated using a dead weight piston gauge [28]. The manganin gauge's electrical resistance, that is, proportional

to the pressure, was measured by a linear unbalanced bridge [29]. Volume changes were calculated from the piston displacement measured by a digital caliper. Corrections related to the expansion of the chamber were evaluated from the Lame equations. Temperature was kept constant by a thermostatic water bath at 293 K. The sample density under normal conditions was determined by weighting known volume of the sample. Since the mass of the sample was not changed during the experiment, the variation of the volume allowed determining the density.

Sound velocity was determined based on time of flight of ultrasonic waves between transducers. Two 5 MHz LiNbO$_3$ (Y36 cut) plates (Boston Piezo-Optics Inc., USA) were used as the transmitter and the receiver. The ultrasonic transducers' mounting has been designed to provide a low level of parasitic ultrasonic signals. The TB-1000 pulser–receiver computer card (Matec, USA) was a signal source for the transmitter. Having passed through the investigated sample, the signal was detected by the receiver and was then processed by the PDA-1000 digitizer card (Signatec, USA). To increase the signal-to-noise ratio, each single measurement was repeated 1024 times and finally averaged. The cross-correlation method [30] was used to evaluate the time of flight. The experimental set-up and method are presented in detail in [19,20]. The pressure was increased in 10 MPa steps and with a time interval which allowed the sample to reach the thermodynamic equilibrium. At a pressure of 210 MPa (at 293 K), a longer relaxation time was used, because at this point the phase transition was found. Subsequently, the pressure was again raised in steps up to 500 MPa and finally it was slowly reduced.

## 3. Investigated sample

Precise analysis of the DAG sample composition was done at the Laboratory of Institute of Agricultural and Food Biotechnology (Department of Meat and Fat Technology) using the Gas Chromatography method. For this purpose, a HP6890 device was applied following the AOCS Cd 11b-91 official method. The analysis was performed according to ISO 5508 and ISO 5509 norms, whereas the data were analysed with ChemStation a 03.34 software. The main components of the investigated DAG are given in Table 1.

Apart from the main components given in Table 1, the slight amounts of other fatty acids at the level of about 0.1%, were presented in the sample, *i.e.* C14:0, C17:0, C17:1, C22:0 and C24:1. But their influence on the observed effects was considered to be negligible.

## 4. Results and discussion

During the experiment, the volume variations and sound velocity were measured simultaneously over a pressure range. It was noticed that at a pressure about 210 MPa, the dependence of sound velocity versus pressure has a discontinuity that is characteristic for the first-order phase transition. Above the transition pressure, the observed dependence of volume on pressure is very similar to that observed in triolein [4]. The changes in sound velocity caused by the increase of pressure are shown in Figure 1. At a phase-transition pressure, the discontinuous increase of the speed of sound was noticed, despite the drop of pressure. Similar phenomena were observed in all previously studied triglycerides [19,20]. At a pressure of 400 MPa, the speed of sound is almost twice greater compared to its value at atmospheric pressure. Such value, *i.e.* about 3000 m/s, is typical for solids, which supports the hypothesis that the crystallization process of triglycerides observed in model triglycerides triolein and trilaurin by Ferstl occurs [10]. During the pressure reduction hysteresis of sound velocity and volume, changes have been observed [19]. This phenomenon reflects the coexistence of two phases during the decompression.
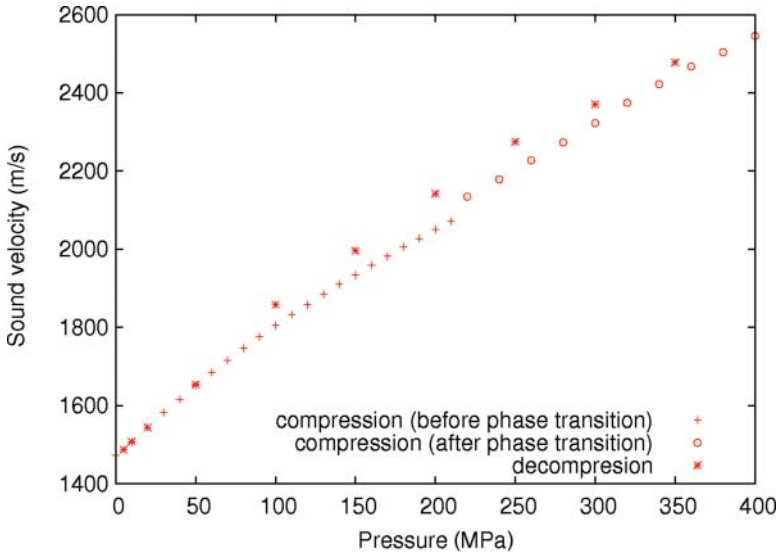
Figure 1.  Sound velocity in the DAG sample in increasing and decreasing pressure.
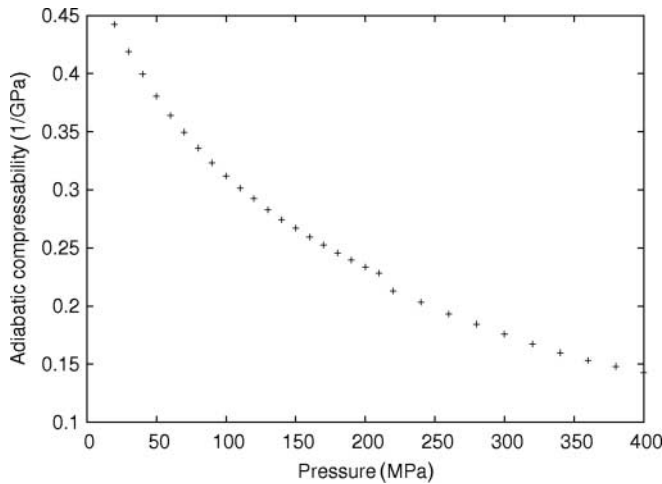


Figure 2.  Adiabatic compressibility versus pressure.

The density, and adiabatic compressibility were evaluated. The dependence of adiabatic compressibility on pressure is shown in Figure 2. As could be noticed, the compressibility after the phase transition is much smaller. The dependence on pressure seems to be weaker.

The elastic properties of materials can also be found from the analysis of sound velocity [31,32]. For this purpose the dependence:

$$v = \sqrt{\frac{K}{d}},$$

where $K$ is the bulk modulus, $d$ the density and $v$ the compressional sound velocity, should be used for liquids whereas for solids it should be replaced by
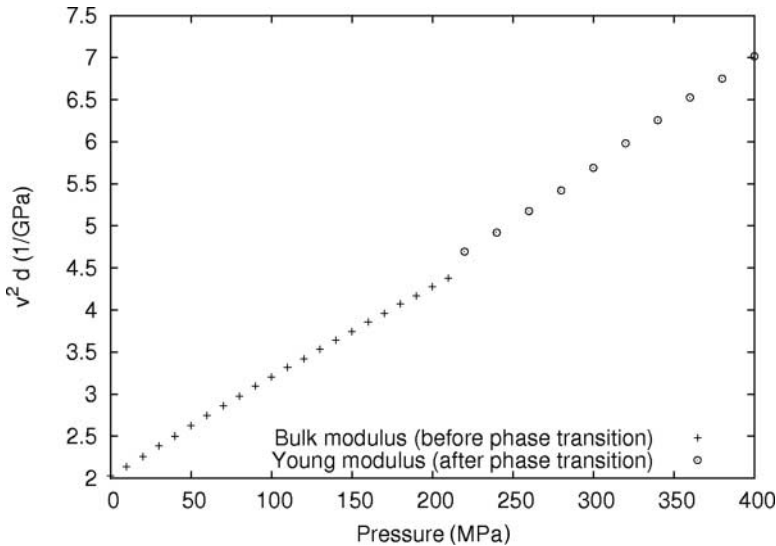
$$v = \sqrt{\frac{E}{d}},$$

Figure 3.   Bulk modulus (liquid state) marked by crosses and Young modulus (solid state) marked by open circles.

where $E$ is the Young modulus. Thus, for both phases, the factor $v^2d$ could be calculated. This factor is equal to $K$ for liquids and to $E = K_s + 4G/3$ for the crystal state, where $G$ is the shear modulus.

Bulk modulus (for liquid) and Young modulus (for crystal state) are shown in Figure 3.

## 5.   Conclusions

(1) Both volume on pressure and sound velocity on pressure dependence have confirmed the existence of phase transition in DAG oil.
(2) The transition pressure is much lower than in TAGs [33]. Molecular differences between both components should be considered as the main reason of the transition's pressure divergence.
(3) The adiabatic compressibility is clearly higher before the phase change. After the change, the compressibility has a weaker dependence on pressure. This trend is visibly reflected by the bulk and Young modulus.
(4) During the pressure reduction hysteresis of sound velocity and volume changes has been observed. This phenomenon reflects the coexistence of two phases during the decompression.

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