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Viscosity and compressibility of diacylglycerol under high pressure[†]

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The influence of high pressure on viscosity and compressibility of diacylglycerol (DAG) oil has been presented in this paper. The investigated DAG oil was composed of 82% of DAGs and 18% TAGs (triacylglycerols). The dynamic viscosity of DAG was investigated as a function of the pressure up to 400 MPa. The viscosity was measured by means of the surface acoustic wave method, where the acoustic waveguides were used as sensing elements. As the pressure was rising, the larger ultrasonic wave attenuation was observed, whereas amplitude decreased with the liquid viscosity augmentation. Measured changes of physical properties were most significant in the pressure range near the phase transition. Deeper understanding of DAG viscosity and compressibility changes versus pressure could shed more light on thermodynamic properties of edible oils.

Keywords: DAG viscosity; compressibility; phase transitions; transmitted and scattered light

Introduction

Viscosity is one of the most important parameters that characterizes properties of any liquid. Knowledge of the viscosity of glycerols is of use for food engineering. Understanding of the rheological properties of liquid is important for those technologies. This paper shows a relationship between pressure, viscosity and compressibility change of diacylglycerol (DAG). For this purpose, change of the viscosity coefficient and compressibility under high pressure was investigated. It was part of a more general investigation on the high pressure phase crystallization. In the described experiment, the temperature and the volume, and the viscosity were simultaneously registered during the experiment. Acylglycerols at ambient pressure and at room temperature remain liquid. As the pressure increases, they transform into the crystalline phase. The observed phase transition is a discontinuous conversion, however, we can measure the coefficient of viscosity and the compressibility changes during the experiment. Even after the transition, viscosity is still measurable because only about 20% of the sample turns into solid. [1] The knowledge of glycerol rheological properties under high pressure is essential for many industrial food high

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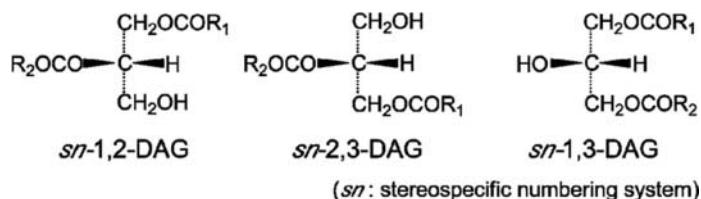


Figure 1. Structure of diacylglycerol.

pressure processes. Most of the classical viscosity measurements are based on falling weights and spinning elements, in general which are difficult to be applied at high pressure. Although rotational viscometers using rotating cylinders or plates have been used for high pressure applications, [2] all of those methods applied to measure viscosity are characterized by low frequency of operation of the vibrating elements and by the presence of moving parts. The measuring process is time-consuming, cumbersome, and does not give reliable results. The measuring equipment has large dimensions and cannot be applied to on-line measurements to monitor the technological process. Moreover, a large quantity of the investigated liquid is necessary to perform the measurements. Thus, the ultrasonic method of measuring viscosity of liquids under high pressure has none of the above-mentioned disadvantages. [3]

Induction time and local temperature during the crystallization process could complement the result of the measurements.

Properties of DAG

A DAG is a glyceride consisting of two fatty acid chains covalently bonded to a glycerol molecule through ester linkages. DAG is an ester of the trihydric alcohol glycerol in which two of the hydroxide groups are esterified with long-chain fatty acids. They can exist in three stereo-chemical forms. DAG is a well-known component of food emulsifiers. DAG consists of a glycerol molecule with two fatty acids bound to it via the ester bonds. Two types of isomers, 1(3),2-DAG and 1,3-DAG, are possible. Because 1(3),2-DAG has an asymmetric carbon atom at position 2, it can exist as *sn*-1,2-DAG and *sn*-2,3-DAG (Figure 1).

A single sample of DAG was investigated. Examined DAG oil [D82T18]AG composed of 82% of DAGs (57.4% of *sn*-1,3 and 24.6% of *sn*-1,2(2,3)) and 18% TAGs (triacylglycerols). The fractions and chemical compositions of fatty acid were examined by the gas chromatography method in which the use of a HP6890 device. Detailed information of fatty acids composition can be found elsewhere. [4]

High pressure phase transition of diacylglycerol oil by means of light transmission and scattering and compressibility changing of DAG, ultrasonic wave viscosity

So far, the observed phase transformations in the DAG at room temperature occurred at pressures of about 200–240 MPa. The phase transitions were measured in the high pressure optical chamber connected to a computer-controlled pump (Figure 2). It gives the possibility of obtaining pressure up to 800 MPa with a controlled rate of pressure increment.

To increase accuracy each experiment was repeated several times (approximately five times).

The experimental setup also consisted of a set of infrared diodes and a set of lock-in type detectors, which allows examination of light in the high pressure chamber while minimizing external interference. Wavelength was chosen in the infrared, because the absorption of light

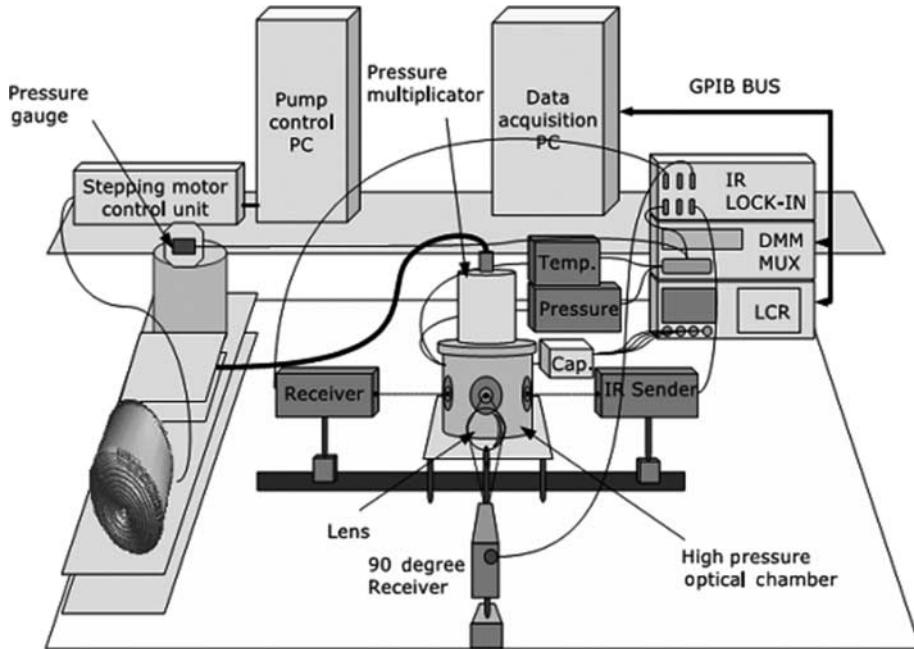


Figure 2. Optical high pressure measurement setup.

by lipids in this region is the smallest. Optical chamber is proper tool for observing changes caused by the phase transition. Experimental setup has the possibility of continuous monitoring of: pressure, temperature, intensity of transmitted light through the sample and the intensity of light scattered at 90° . One of the first indicators of phase transition was a significant decrease in light transmission caused by beginnings of the newly formed crystals. This new solid formations also results in very strong light scattering. Changes in intensities are immediate and very clear (by several orders of magnitude). Compressibility and viscosity changes were measured in the cylindrical chamber, which was working with a hydraulic press. Piston shift was measured with a 0.1 mm resolution. The pressure was monitored by the manganin resistor of $(74.200 \pm 0.002)\Omega$. The chamber was placed in a thermostatic bath, which was connected to the external thermostat (Julabo Labortechnik, Germany). Viscosity measurement was carried out at a pressure up to 400 MPa and a constant temperature 20°C using an ultrasonic setup. As a viscosity sensor, the Bleustain–Gulyaev (B–G) surface acoustic waveguide has been used. The B–G surface wave propagates in the homogeneous waveguide structure. The surface of the piezoelectric ceramics is covered with a very thin metallic layer. B–G waves are shared horizontal surface waves. This is why, by their nature, they are useful for the investigation of the rheological parameters of viscoelastic liquids. [5] The ultrasonics method of measuring viscosity can be treated as another new way of measurement. [6]

Results

The results shed more light on the phase transitions nature. Phase transition was observed in three different experiments. In each of those experiments, high pressure influenced liquid. All high pressure methods have shown almost the same value of the transition pressure. At constant temperature, the crystallization process occurs at the same range of pressure (220 ± 10) MPa.

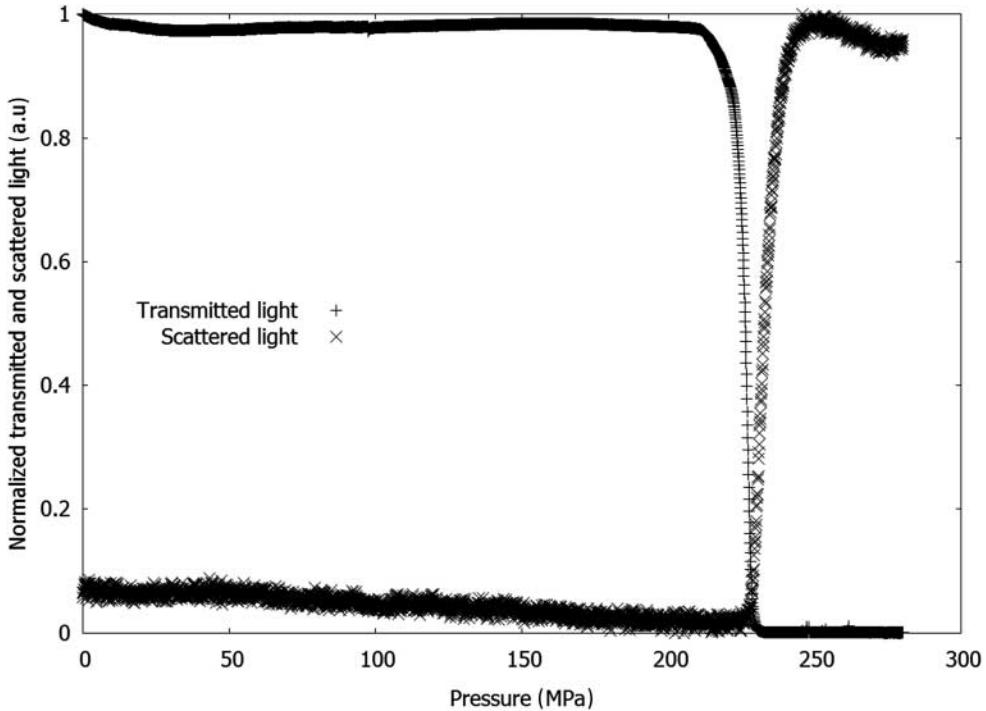


Figure 3. Normalized optical signals versus pressure.

Phase transitions by means of light transmission and scattering

The results of high pressure phase transitions of DAG oil by means of scattered and transmitted light was widely characterized in [4]. The DAG sample was examined at constant temperature 20 °C which was generated by a thermostatic setup. The pressure was generated by a stepper motor-driven pump. Drastic change in intensity of scattered and transmitted light allowed to identify the phase transition and was followed by drop in the pressure, as shown in Figure 3. For a pressure from 0.1 MPa (atmospheric) to 220 MPa intensity of scattered and transmitted beams are on a constant level (~ 1 AU for transmitted, ~ 0 AU for scattered). When compression reaches the transition pressure, the transmitted light intensity rapidly drops to the minimum value and at the same time, the scattered light intensity rises to its maximum. Light intensities change as a result of the compression generated crystallization process which is a characteristic phenomenon associated with solidification. [7]

Compressibility

The change of DAG sample compressibility was measured in a high pressure cylindrical chamber, which was working with a hydraulic press. A digital calliper of sensitivity ± 0.1 mm was used for monitoring the piston shift. Chamber pressure expansion was taken into account during volume change calculations. The experimental data were approximated by Tait's equation. The method was published elsewhere in details. [8] The measurements of piston shift were done for the DAG sample under high pressure. The temperature was constant, when pressure was increased by 10 MPa steps. The estimated values of Tait's coefficients suggest that the high pressure phase is solidified as long as pressure is over the transition threshold. [9] The solidified phase has a smaller volume than the liquid phase.

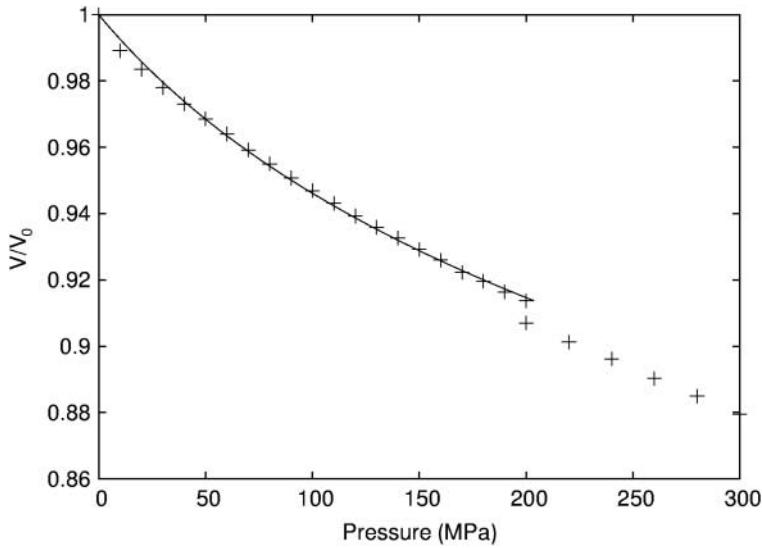


Figure 4. Pressure versus volume changes.

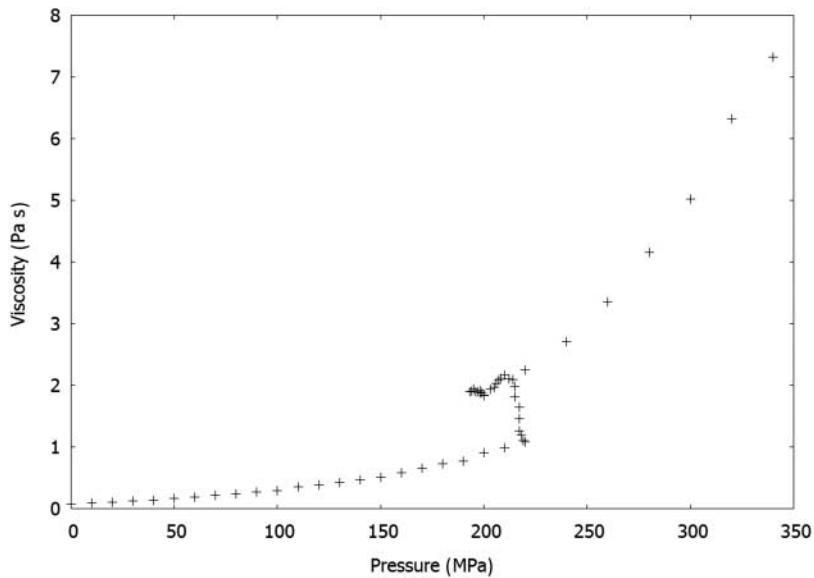


Figure 5. Graphs of diacylglycerol oil viscosity versus pressure.

As shown in Figure 4, the increase in pressure was stopped when phase transitions were observed. The modified Tait's equation of state was used for the evaluation of this data.

$$\frac{V}{V_0} = 1 - C \ln \left(1 + \frac{p}{B} \right),$$

where V is the volume, V_0 the initial volume, p the pressure, and B and C are the fitted coefficients. Obtained values of coefficients for DAG sample are: $C = (0.0774 \pm 0.0039)$, $B = (99.8639 \pm 7.6560)$ MPa. The crystal phase has a smaller volume than the liquid phase.

Viscosity

The DAG high pressure viscosity is shown in Figure 5. The pressure was generated by a hand pump in 10 MPa steps, during the phase transition which occurs at approximately 210 MPa. Then pressurization was kept until viscosity and compressibility changes suggest that the high pressure phase is solidified. An ultrasonic method, which uses the surface acoustic B–G wave, was described elsewhere. [10]

The occurrence of phase transition is accompanied by the discontinuity in the plot of the liquid's viscosity as a function of pressure. During the phase transition, the hydrostatic pressure decreases while the viscosity value substantially increases. The pressure was increased until the phase transition began (first part of each curve in Figure 5). The viscosity was increasing almost exponentially during transition. The graph of the DAG sample viscosity as a function of pressure shows a discontinuity that indicates the presence of phase transitions.

Conclusions

The main aim of the research was to measure the influence of high pressure on DAG oil. A DAG sample was researched under high pressure conditions. The phase transition in the DAG sample has occurred in all three physical experiments performed. Changes of pressure, compressibility and viscosity suggest that the high pressure phase is solidified. Diagrams of normalized transmitted and scattered light give characteristic phenomena associated with the crystallization process. Graphs of the DAG sample viscosity and compressibility as a function of pressure show a discontinuity that indicates the presence of phase transition. All measurements showed that for solidification of DAG at 20 °C, the transition pressure is approximately 210 MPa.

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