



Investigation of high-pressure phase transitions in DAG (diacylglycerol) oil using the Bleustein–Gulyaev ultrasonic wave method

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ABSTRACT

In this paper, phase transitions in diacylglycerol (DAG) oil are investigated by using an ultrasonic method for measuring viscosity. Viscosity of diacylglycerol (DAG) oil is measured over a wide range of hydrostatic pressures up to 500 MPa, and at temperatures ranging from 10 to 40 °C. The observed discontinuities in the viscosity versus pressure curves (isotherms) indicate phase transitions. An original ultrasonic method that uses the surface acoustic Bleustein–Gulyaev (B–G) wave was employed to measure the viscosity of DAG oil at high pressure range. This method allows for the fast and reliable measurement of DAG oil viscosity along various isotherms. Moreover, the kinetics of the observed phase transformations at various temperatures was analyzed. The results of the study are a novelty, and can be helpful in evaluating the physicochemical properties of edible oils.

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1. Introduction

Edible oils are an important component of human diet because they provide nutritional properties, flavor and texture (consistency) of food. Knowledge of their composition and physical properties of their compounds is indispensable. In this paper, we analyze the physicochemical properties of Diacylglycerol (DAG) oil, which is an important compound of fatty food products. For example, olive oil can have DAG content up to 5–6% (Shimizu et al., 2008). Similar content of DAG appears in palm oil. In sunflower, sesame, rapeseed, corn, cottonseed and peanut oils the DAG content is equal to 2–3%. DAG is also a compound of solid animal fats, e.g. lard and tallow (D'Alonzo, Kozarek, & Wade, 1982). The consumption of DAG oil is claimed to have beneficial effects on obesity and weight-related disorders (Lo, Tan, Long, Yusoff, & Lai, 2008), and is recommended by dietitians. Moreover, DAG oil is also applied in the pharmaceutical industry.

During food manufacture, processing and conservation high-pressure methods are often used. Various food products (fruits, vegetables, oils, meat, fish, dairy products) are preserved applying high pressure technology (HPT). After high-pressure processing these products maintain the nutritional and sensory qualities for longer time. Hydrostatic pressures used in HPT range from 100 to 800 MPa. For example, olive and seed oils are subjected to a pressure of 700 MPa, potatoes – 400 MPa, fruit juices – 350 MPa, ham – 300 MPa, and fresh beef – 800 MPa (Kadam, Jadhav, Salve, & Machewad, 2012). Commercial food pressurization is

applied among others in Japan, USA, France and Spain. Our experiments were performed in the pressure range from atmospheric up to 500 MPa. Pressures used in food pressurization are of the same order. Phase transitions that occur during the pressurization of food have a very significant effect. Phase transformations may also be accompanied by drastic changes of the physicochemical and mechanical properties of the food (LeBail et al., 2003).

The viscosity of the liquid is a physical parameter whose value undergoes significant changes during phase transitions. Viscosity measurement is an important component of many quality control and process monitoring procedures in food processing. On-line monitoring of viscosity enables one to control precisely successive operations in food processing. Many applications of process viscometry in food processing have been reported, e.g. in processing of milk, soups, sauces, ketchups, yogurts, fruit juices, mayonnaises, chocolates, and in cheese production (Cullen, Duffy, O'Donnell, & O'Callaghan, 2000). Therefore, in this paper we report measurements of DAG oil viscosity over a wide range of hydrostatic pressures up to 500 MPa and at temperatures ranging from 10 to 40 °C.

The presence of phase transition is characterized by the discontinuity in the plot of liquid viscosity as a function of pressure. During the phase transition, the hydrostatic pressure decreases, while the viscosity value substantially increases. Phase transition region separates the regions of low-pressure phase and high-pressure phase.

Viscosity measurements in high-pressure range, especially during phase transitions, are very difficult. Traditional mechanical methods of viscosity measurements are almost useless in this case.

To overcome the disadvantages of the mechanical methods ultrasonic methods that use the bulk shear acoustic waves were applied

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(Kielczyński, Pajewski, & Szalewski, 2002, Kulisiewicz, Baars, & Delgado, 2007, Kulisiewicz & Delgado, 2010).

Ultrasonic methods are also widely used for food research (Bamberger & Greenwood, 2004, Saggin & Coupland, 2001, Koc & Vatandas, 2006, Benedito, Garcia-Pérez, Dobarganes, & Mulet, 2007, Santacatalina, Garcia-Pérez, Benedito, & Corona, 2011, Scanlon, 2004). These methods are nondestructive. Moreover, they can be applied on-line in food industry.

The ultrasonic method for measuring the viscosity of liquids at high pressure presented in (Kulisiewicz et al., 2007, Kulisiewicz & Delgado, 2010) uses the propagation of the bulk shear acoustic wave in an investigated liquid. The bulk shear acoustic waves propagate at a very small distance into a viscous liquid. This is the reason that the above mentioned method is very complicated and difficult in the practical use.

Therefore, to measure the viscosity of liquids at high pressure, we applied an original ultrasonic method that uses shear acoustic surface waves of the Love and Bleustein–Gulyaev type (Kielczyński, Szalewski, Siegoczyński, & Rostocki, 2008). This method is very efficient and can relatively easily and quickly measure the viscosity of liquids at high pressure region.

We have investigated DAG oil composed of 82% of DAGs and 18% of triacylglycerols (TAGs), with a vestigial content of monoacylglycerols (MAGs) and free fatty acids. The fractions were determined by means of the gas chromatography method using a HP6890 device, and the analysis was conducted following the AOCS Cd 11b-91 method. The composition of fatty acids is presented in Table 1. The analysis was performed according to the ISO 5508 and ISO 5509 norms.

Original ultrasonic measuring method and measuring setup are presented in Section 2. A Bleustein–Gulyaev surface acoustic wave waveguide is used as a viscosity sensor.

Experimental results are presented in Section 3. To the authors' best knowledge, such results have not been published as yet in the scientific literature.

The kinetics of phase transitions was also investigated. The results of measurements are presented in Section 4.

2. Ultrasonic measurement method

The Bleustein–Gulyaev (B–G) surface wave propagates in the waveguide structure presented in Fig. 1. The surface of a piezoelectric ceramic is covered with a very thin metallic layer that cancels the electric field on that surface ($x_1 = 0$). Piezoelectric ceramic is polarized along the x_2 axis. The B–G wave is a shear horizontal (SH) surface wave having only one component of mechanical displacement u_2 perpendicular to the direction of propagation x_3 and parallel to the surface. The B–G wave is a nondispersive wave, i.e. its phase velocity does not depend on frequency.

Table 1

Fatty acids in the investigated DAG oil according to ISO-5508.

Fatty acid (carbon atoms: C=C bonds)	Amount [%]
C14:0	0.1
C16:0	4.5
C16:1 (Σ)	0.5
C17:0	0.1
C17:1	0.1
C18:0	2.5
C18:1 (Σ c)	59.1
C18:2 (cc)	19.6
C18:3(ccc)	8.9
C20:0	1.9
C20:1 (Σ)	1.0
C22:0	0.1
C22:1 (Σ)	1.2
C24:0	0.3
C24:1	0.1

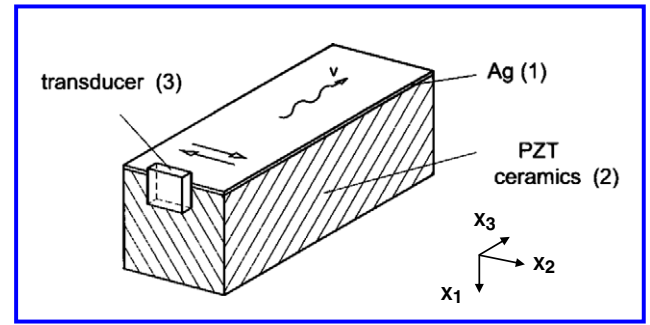


Fig. 1. Waveguide of the Bleustein–Gulyaev wave. Piezoceramic PZT waveguide (2) is covered on the surface by a very thin metallic (Ag) layer (1). Surface acoustic (B–G) wave is excited by means of the PZT plate transducer (3). PZT ceramics (both in the transducer and waveguide) is polarized along the axis x_2 .

Bleustein–Gulyaev (B–G) wave velocity depends only on the mechanical parameters (i.e., shear modulus and density) of PZT piezoelectric ceramics, from which the waveguide is made. In the considered frequency range (the range of several MHz), these parameters for PZT ceramics are independent of frequency, therefore the B–G wave is nondispersive (Royer & Dieulesaint, 2000). The amplitude of the B–G wave is localized in the vicinity of the waveguide surface and diminishes when the distance x_1 from the waveguide surface into the bulk increases. The penetration depth of the B–G wave is of the order of a wavelength. Consequently, the energy of the B–G waves is mostly concentrated in the vicinity of the surface of a piezoelectric ceramic waveguide used as a viscosity sensor.

The liquid covering the waveguide surface loads it mechanically. The value of this load is proportional to the value of the mechanical impedance Z of the liquid. The mechanical impedance of a liquid loading the surface of the B–G wave waveguide is equal to the characteristic shear impedance of the liquid Z_L for plane waves:

$$Z_L = (\rho_L \cdot G_L)^{1/2} \quad (1)$$

where $G_L = G_L' + jG_L''$ is the complex shear modulus of the liquid defined as the ratio (T/S) of the shear stress T to the shear strain S , ρ_L is the liquid density and $j = (-1)^{1/2}$.

By applying the perturbation method (Auld, 1973), one can prove that the change in the complex propagation constant γ of the B–G wave produced by viscoelastic liquid loading is as follows (Kielczyński, Pajewski, Szalewski, & Balcerzak, 2004):

$$\Delta\gamma = -j \left(\frac{|u_2|_{x_1=0}^2}{4 \cdot P} \right) \cdot Z_L = -j \cdot K \cdot Z_L \quad (2)$$

where: u_2 is the non-perturbed B–G wave amplitude on the waveguide surface, P is the mean power on the unit width of the non-perturbed B–G wave. The coefficient K is the characteristic quantity for each B–G wave waveguide and depends solely on the material parameters of the waveguide and frequency (Kielczyński & Płowiec, 1989).

For the case of a Newtonian (viscous) liquid, the shear mechanical impedance can be expressed as follows:

$$Z_L = R_L + jX_L = \left(\frac{\rho_L \omega \eta}{2} \right)^{1/2} (1 + j) \quad (3)$$

where: η is the viscosity of a liquid, and ω is an angular frequency.

Thus, employing Eq. (3) we can write (Kielczyński et al., 2008):

$$\eta = \frac{2R_L^2}{\omega \rho_L} = \frac{2X_L^2}{\omega \rho_L} \quad (4)$$

where: R_L and X_L are the real and imaginary parts of the mechanical shear impedance of a liquid. For a Newtonian liquid $R_L = X_L$.

The shear mechanical impedance of a liquid Z_L can be determined from the measurements of the change in the attenuation of wave trains that propagate in the waveguide loaded by the liquid (Kielczyński et al., 2004).

2.1. Measuring setup

The experimental setup for measuring the viscosity of liquids under high pressure at various temperatures is presented in Fig. 2. High pressure was generated in a thick-walled cylinder chamber with a simple piston and Bridgman II sealing system. The piston–cylinder assembly was working with a hydraulic press, driven by a hand-operated pump. The piston displacement was controlled by a digital caliper. For pressure measurements a 100 Ω manganin transducer was used. Its resistance was measured with a linear unbalanced resistance bridge (Rostocki & Wiśniewski, 1977). The pressure transducer was calibrated using a dead weight piston gage (Rostocki, Urbański, Wiśniewski, & Wilczyńska, 2005). The temperature in the chamber was measured using T-type thermocouple (Cu-constantan). A thermostatic bath was circulating in a thermostatic jacket around the chamber. The thermostatic jacket was connected to a precision thermostat (Julabo Labortechnik, Germany) working as a refrigerated/heating circulator. The viscosity sensor (B–G waveguide) was placed inside the high-pressure chamber. The piezoelectric transducer attached to the B–G wave waveguide, manganin coil, and thermocouple was connected with the external measuring setup by an electrical multichannel lead through.

The sending–receiving piezoelectric transducer, attached to the B–G wave waveguide, was driven by the TB-1000 pulser–receiver computer card (Matec, USA). The TB-1000 pulser generated the rf tone bursts with a frequency $f = 2$ MHz and length equal to 0.5 μ s. The repetition period was equal to 0.4 ms. The B–G wave impulse generated by the transducer was reflected in multiple ways between two opposite edges of the B–G wave waveguide. The signals received by the transducer were amplified by the TB-1000 receiver and sent into the PDA-1000 digitizer card (Signatec, USA). This card sampled and digitized the input analog signals. The stored signals were then analyzed by computer software. For each measurement, the ultrasonic signal was averaged 1024 times in order to improve the signal-to-noise ratio.

3. Experimental results

The plots of measured DAG oil viscosity as a function of pressure, at various temperatures, are shown in Fig. 3. The pressure was generated

in 10 MPa steps, then kept constant for about 5 min. During that time the pressure and temperatures were observed. That allowed the detection of the pressure drop due to phase transition and the observation whether the system was reaching thermodynamic equilibrium. The viscosity of DAG oil was measured as a function of pressure and temperature at 10 °C intervals from 10 °C to 40 °C and from atmospheric pressure to 500 MPa. In Fig. 3 three different parts of each curve can be seen. At first the pressure was increased until the first-order phase transition began (first part of each curve in Fig. 3). The viscosity was increasing almost exponentially according to known empirical Barus formula $\eta(p) = \eta_0 \cdot \exp(\alpha p)$, where η_0 is the viscosity at atmospheric pressure and α is the viscosity–pressure coefficient. One can see in Fig. 3 that the coefficient α depends on temperature. The observed spontaneous pressure drop indicates initiation of the phase transition. When the phase transition started we stopped the compression, and the piston in the high-pressure chamber was fixed to enable the phase transition to occur undisturbed. During the phase transition a pressure drop was observed in the chamber. The viscosity showed the further rise despite the pressure drop (second part of each curve in Fig. 3). When the temperature during measurements was higher, the pressure, at which the phase transition began, increased (e.g. 140 MPa for 10 °C and 420 MPa for 40 °C). Consequently, the pressure at which transition stopped was also higher. The stabilization of pressure and negligible changes in viscosity indicate that the phase transition is completed. At the termination of the phase transition process the pressure was increased again, in order to measure the viscosity of the new high-pressure phase of DAG oil (third part of each curve in Fig. 3). The further increase of viscosity with increasing pressure was observed. With the increase of temperature, the viscosity of DAG oil high-pressure and low-pressure phases diminishes, see Fig. 3. For the temperature 50 °C phase transition ran very slowly and the changes of viscosity and pressure were very small.

4. Kinetics of phase transitions

The kinetics of the phase transition was investigated during viscosity measurements, see Fig. 4. Pressure changes, occurring during phase transition, were registered with the piston locked in a fixed position. At first the pressure remained constant. Subsequently, a monotonic decrease of pressure (at practically constant volume) was observed, due to a phase transition in DAG oil. Finally, the pressure level stabilized. This means that the phase transition was complete. As a result, a new high-pressure phase in DAG oil, with a more dense arrangement of molecules, has emerged. Physical properties (viscosity and density) of the new high-pressure phase are different than those in the

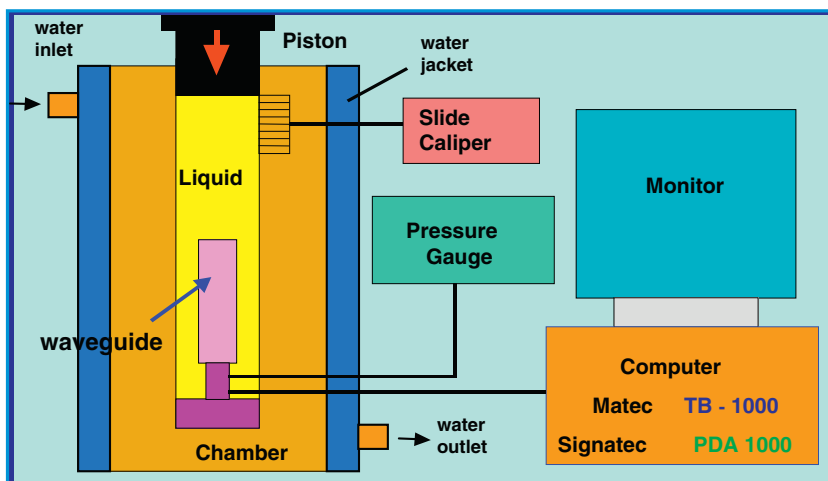


Fig. 2. Ultrasonic setup for measuring the viscosity of liquids under high pressure. Temperature of water is stabilized by refrigerated/heating circulator (not presented in the graph).

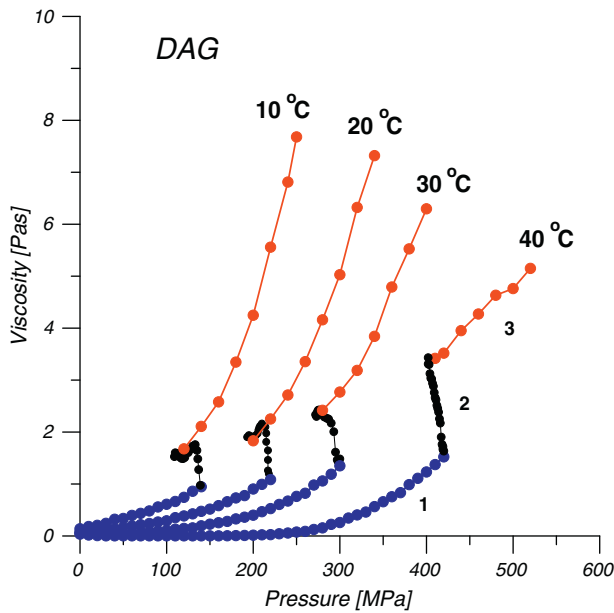


Fig. 3. Graphs of diacylglycerol oil viscosity as a function of pressure along various isotherms ($T = 10, 20, 30,$ and $40\text{ }^{\circ}\text{C}$). (1) refers to low-pressure phase, (2) indicates the phase transition, and (3) refers to high-pressure phase. $f = 2\text{ MHz}$.

low-pressure phase. One can see in Fig. 4, that with the increase of temperature phase transition starts at higher value of pressure. Moreover, an augmentation in temperature decreases the speed of phase transition (e.g., phase transition at $40\text{ }^{\circ}\text{C}$ runs about 45 min). On the other hand, with the decrease in temperature, phase transition starts at a lower value of pressure and runs with higher speed (e.g., phase transition at $10\text{ }^{\circ}\text{C}$ runs about 15 min).

Up to now the kinetics of the phase transition in DAG oil was investigated only at room temperature by means of light transmission and scattering (Kościeszka et al., 2012).

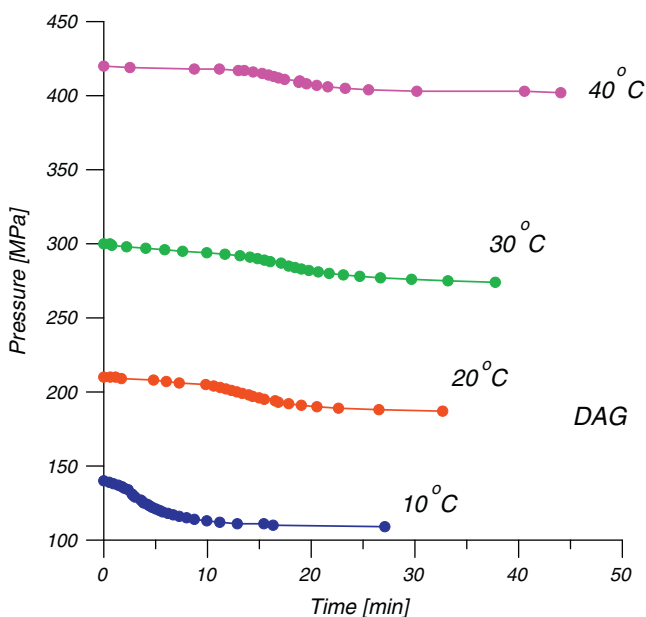


Fig. 4. Kinetics of phase transition in diacylglycerol oil at various temperatures ($T = 10, 20, 30,$ and $40\text{ }^{\circ}\text{C}$).

5. Conclusions

In this work, viscosity measurements of diacylglycerol (DAG) oil in a wide range of hydrostatic pressure up to 500 MPa, and for various values of temperature (isotherms) were presented. The Bleustein–Gulyaev surface acoustic wave method was used to measure the viscosity of DAG oil at high pressure. Graphs of DAG oil viscosity as a function of pressure show a discontinuity, that indicates the presence of phase transitions.

Application of the ultrasonic Bleustein–Gulyaev wave method enabled both the detection of phase transitions in DAG oil and investigation of their kinetics. This ultrasonic B–G wave method is a general method and can also be used to investigate phase transitions in a wide spectrum of food products and substances of biological origin, among other edible oils and fats.

To the author's knowledge, the measurements of DAG oil viscosity under high pressure, during the phase transitions have not been reported in the scientific literature.

The investigation of phase transitions is very important in high-pressure food processing and conservation. Phase transformations can modify significantly the molecular structure and, consequently, affect the texture and sensory characteristics of food products. Therefore, measuring the viscosity of the liquid at high pressure is important in assessing the quality of food products subjected to high pressure technological processes.

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