

Application of the Bleustein-Gulyaev wave method for investigation of high-pressure phase transitions in diacylglycerol oil

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Abstract – Phase transitions in diacylglycerol (DAG) oil were investigated by using an ultrasonic method for measuring viscosity. Viscosity of DAG oil was 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 allowed for fast and reliable measurement of DAG oil viscosity along various isotherms. Moreover, the kinetics of the observed phase transformations at various temperatures was analyzed

Keywords: Viscosity, Bleustein-Gulyaev waves, high pressure, phase transitions

I. INTRODUCTION

Diacylglycerol (DAG) is an important compound of fatty food products. During food manufacture, processing and conservation high-pressure methods are often used [1]. Various food products (fruits, vegetables, oils, meat, fish, dairy products) are preserved applying high pressure technology. After high-pressure processing these products maintain the nutritional and sensory qualities for longer time. Phase transitions that occur during the pressurization of food are very significant effect. Phase transformations may be accompanied by drastic changes of the physicochemical and mechanical properties of the food [2]. 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 to control precisely successive operations in food processing. Many applications of process viscometry in food processing have been reported [3]. 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. Pressures used in food pressurization are of the same order. The kinetics of phase transitions was also investigated.

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.

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. Therefore, to measure the viscosity of liquids at high pressure, we applied an original ultrasonic method that uses shear acoustic surface waves of the Bleustein-Gulyaev type [5-7]. The sensor consists of the B-G wave waveguide made of PZT piezoceramics and sending-receiving PZT transducer. The operating frequency was 2 MHz. This method is very efficient and can relatively easily and quickly measure the viscosity of liquids at high-pressure region.

II. MEASURING METHOD AND SETUP

The experimental setup for measuring the viscosity of liquids under high pressure at various temperatures is presented in Fig.1. High pressure was generated in a thick-walled cylinder chamber with a simple piston and Bridgman II sealing system. The piston displacement was controlled by a digital caliper. For pressure measurements a typical 100 Ω manganin transducer was used. Its resistance was measured with a linear unbalanced resistance bridge [4]. 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.

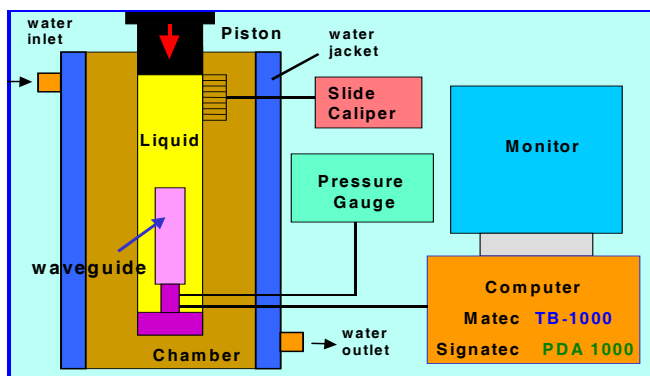


Fig.1. Ultrasonic experimental setup for measuring the viscosity of liquids under high pressure at various temperatures. Temperature of water is stabilized by refrigerated/heating circulator (not presented in the graph).

The viscosity sensor (B-G waveguide) was placed inside the high-pressure chamber. The piezoelectric transducer attached to the B-G wave waveguide, manganine coil, and thermocouple were connected with the external measuring setup by an electrical multichannel lead through.

The sending-receiving piezoelectric PZT 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. A computer program that controlled the operation of the computer cards and data acquisition was written in C++ language

III. EXPERIMENTAL RESULTS

A. VISCOSITY

Figure 2 shows the results of high-pressure viscosity measurements of DAG oil at various temperatures. The pressure was generated in 10 MPa steps, then kept constant for about 5 minutes. During that time the pressure and temperature was observed. That allowed identification of the pressure drop due to phase transition and to observe whether the system was reaching thermodynamic equilibrium. The viscosity of DAG oil was measured as a function of pressure and temperature at 10 $^{\circ}$ C intervals from 10 $^{\circ}$ C to 40 $^{\circ}$ C and from atmospheric pressure to 500 MPa and controlled by the T-type thermocouple. In the Fig.2 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 $\eta(p) = \eta_0 \exp(\alpha p)$, where η_0 is the viscosity at atmospheric pressure and α is the viscosity-pressure coefficient. One can see in Fig. 2 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. 2). It means that the volume occupied by the resulting high-pressure phase diminished. When the temperature during measurements was higher, the pressure, at which the phase transition began, increased, see Fig. 2. Consequently, the pressure at which transition stopped was also higher. The stabilization of pressure and negligible changes in viscosity indicate that 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. 2). The further increase of viscosity with increasing pressure was observed.

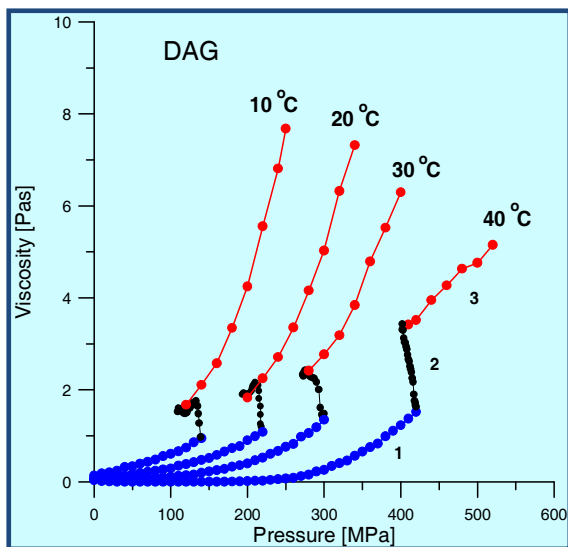


Fig.2. Viscosity of DAG oil versus pressure along various isotherms ($T = 10, 20, 30,$ and $40\text{ }^{\circ}\text{C}$).

With the increase of temperature, viscosity of DAG oil low-pressure and high-pressure phases diminishes, see Fig.2.

B. KINETICS

The kinetics of the phase transition was investigated during viscosity measurements, see Fig. 3. 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 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 low-pressure phase.

One can see in Fig.3, 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.

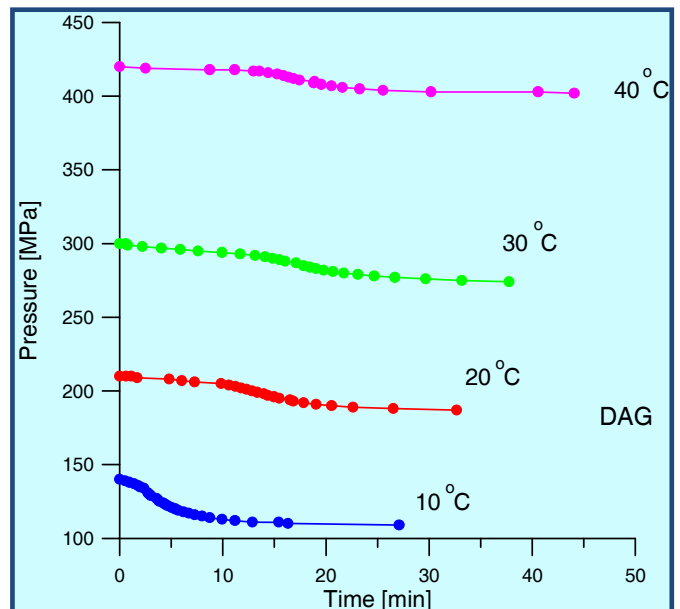


Fig.3. Kinetics of phase transition in DAG oil at various temperatures ($T = 10, 20, 30,$ and $40\text{ }^{\circ}\text{C}$).

IV. 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 others edible oils and fats.

To the authors' knowledge, the measurements of DAG oil viscosity under high pressure, during the phase transition, have not been reported in the scientific literature. The kinetics of the phase transition in DAG oil was investigated only at room temperature by means of light transmission and scattering [8].

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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