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Ultrasonic investigation of physicochemical properties of liquids under high pressure

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***Abstract* – High pressure research of the physicochemical properties of liquids has been stimulated by the fast development of such technologies as biodiesel production, high-pressure food processing and conservation, modification of biotechnological properties. Monitoring and studying liquid viscosity and ultrasonic wave velocity in liquids as a function of pressure and temperature enable to evaluate many important physicochemical parameters of liquids. These methods allow also insight into the phenomena governing the microstructural modifications occurring in treated substances, i.e. phase transitions. The knowledge of physicochemical properties (e.g. density, relaxation time, internal pressure or free volume) of pressurized substances is essential for understanding, design and control of the process technology. Measurements were conducted on the example of diacylglycerol oil (DAG oil), that is an important constituent of oils and fats.**

Keywords: Ultrasonic velocity, viscosity, high pressure, free volume ,relaxation time, internal pressure

I. INTRODUCTION

High pressure methods are often used during food manufacture, processing and conservation. The knowledge of physicochemical properties of pressurized substances, and their changes as a function of pressure and temperature, is necessary for mathematical modeling, design and control of the process technology. There is very little data concerning these properties [1].

Direct measurements of the physicochemical properties of liquids are very difficult under conditions of high pressure. The sound velocity is closely linked with these properties and can be measured relatively easily and with high accuracy over wide ranges of pressure and temperature. Measurements of liquid viscosity versus pressure and temperature is also necessary to calculate physicochemical properties of liquids. Classical mechanical methods of viscosity measurements are almost useless in high-pressure range. To this aim ultrasonic methods can be applied.

We have investigated diacylglycerol (DAG) oil composed of 82% of DAGs and 18% of triacylglycerols (TAGs), with a vestigial amount of monoacylglycerols (MAGs) and free fatty acids. The fractions were determined by means of the gas chromatography method. DAG is an important constituent of oils and fats [2].

To measure the viscosity of liquids at high pressure, we applied one of the ultrasonic methods, developed in the Institute of Fundamental Technological Research, that uses shear acoustic surface waves of the Bleustein-Gulyaev (B-G) type [3-6]. The sensor consists of the B-G wave waveguide made of PZT

piezoceramics and sending-receiving PZT transducers. The details of the measuring method and setup are presented in [7,8].

For measurements of the phase velocity of longitudinal ultrasonic waves, the authors have constructed the computerized setup especially designed to obtain a low level of parasitic ultrasonic signals. A special mounting of transducers in the high-pressure chamber was fabricated. The measuring setup is described in [9,10]. The time of flight of the ultrasonic pulses was evaluated by applying the cross-correlation method.

II. EXPERIMENTAL RESULTS

Viscosity, sound velocity and density were measured in the pressure range up to 600 MPa, at temperatures 10, 20, 30, 40 °C.

Figure 1 shows the results of high pressure viscosity measurements of DAG oil at various temperatures. In Fig.1 three different parts of each curve can be seen: 1) low-pressure phase of DAG oil, 2) region of phase transition, 3) high-pressure phase of DAG oil [6].

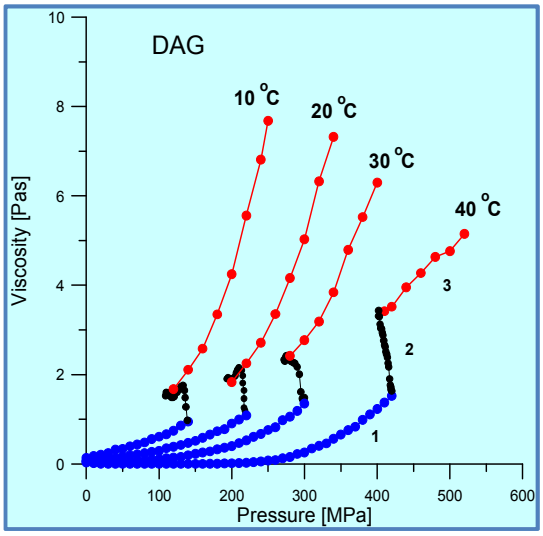

Fig.1. Graphs of diacylglycerol oil viscosity as a function of pressure along various isotherms (T = 10, 20, 30, and 40 ^{0}C). (1) refers to low-pressure phase, (2) indicates the phase transition, and (3) refers to high-pressure phase. f = 2 MHz.

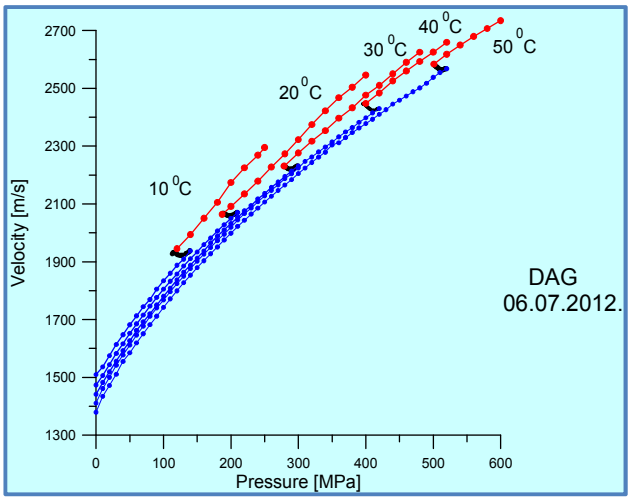

Fig.2. Plots of sound velocity in DAG oil as a function of pressure along various isotherms ($T = 10, 20, 30, 40, and\ 50\ °C$).

The plots of measured longitudinal ultrasonic wave (frequency 2 MHz) velocity in DAG oil as a function of pressure, at various temperatures, are shown in Fig. 2. Similarly as in Fig. 1, we can see three different parts of each curve [9].

During experiments, DAG oil volume changes were measured by observation of piston displacement inside the high-pressure chamber. It was measured by digital caliper gauge. Corrections related to the expansion of the chamber were considered during data analysis. Measured volume changes versus pressure have been used for evaluation of DAG oil density as a function of pressure, at various temperatures.

III. PHYSICOCHEMICAL PROPERTIES OF DAG OIL

Measured values of sound velocity, viscosity and density versus pressure, at various temperatures, have been used to calculate relaxation time, free volume and internal pressure. Calculations have been conducted for low-pressure phase of DAG oil (before phase transition) and for high-pressure phase of DAG oil (after phase transition). During phase transition process two phases of DAG oil exist simultaneously. Moreover there is thermodynamic disequilibrium. For this reason, the physicochemical parameters of the substance cannot be clearly determined.

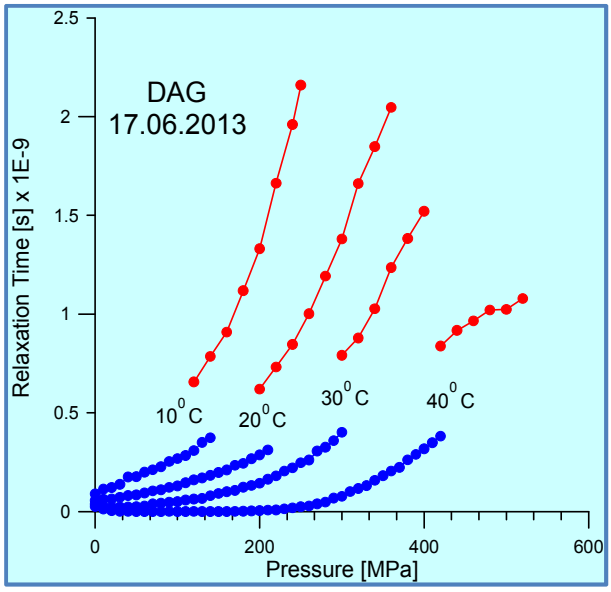

Fig.3. Relaxation time in DAG oil versus pressure at various temperatures.

A. Relaxation time

The viscous relaxation time is connected with measured values of viscosity, sound velocity and density as follows [11]:

$$\tau = 4\eta/3\rho v^2 \qquad (1)$$

where: η - viscosity, ρ - density, v – sound velocity.
Figure 3 presents relaxation time as a function of pressure at various temperatures. The increase of relaxation time with pressure is rather slow for low-pressure phase and very rapid for high-pressure phase.

B. Free volume

Free volume was calculated using the relation [12]:

$$V_j = (Mv/K\eta)^{3/2} \qquad (2)$$

where: M is molecular weight, K – temperature independent constant, $K = 4.28 \cdot 10^9$ for all liquids.
Free volume as a function of pressure, at various temperatures, is presented in Fig. 4.

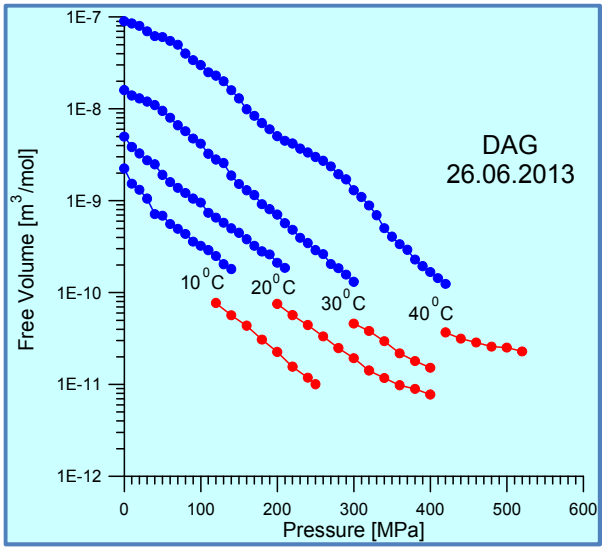

Fig.4. Free volume in DAG oil as a function of pressure at various temperatures.

Free volume decreases with pressure and increases with temperatures.

C. Internal pressure

Internal pressure was evaluated using the equation [13]:

$$P_i = bRT \cdot (K\eta/v)^{1/2} \cdot \rho^{2/3}/M^{7/6} \qquad (3)$$

where: b - packing factor, R - universal gas constant, T – temperature in Kelvin.

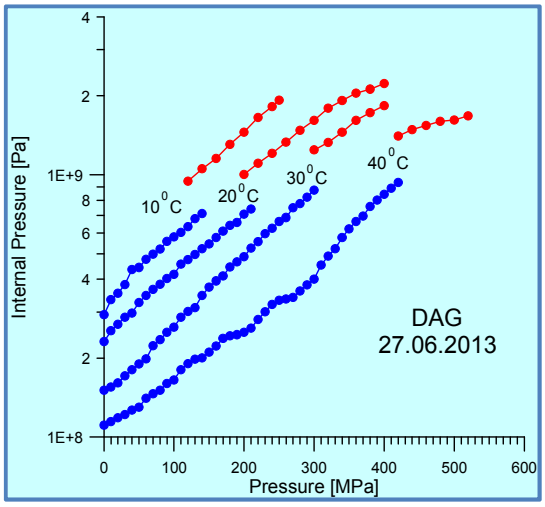

Fig.5. Internal pressure in DAG oil versus pressure along various isotherms.

Fig. 5 presents internal pressure as a function of pressure, at various temperatures. Internal pressure increases with external pressure and decreases with temperature.

IV. CONCLUSIONS

In this work physicochemical properties (relaxation time, free volume, internal pressure) of DAG oil have been determined using measured values of viscosity and longitudinal acoustic wave velocity. The Bleustein-Gulyaev wave method was used to measure the viscosity of DAG oil in pressure range from atmospheric up to 600 MPa, at temperatures 10, 20 ,30 ,40 °C. The sound velocity in DAG oil was measured in the same ranges of pressure and temperature.

The knowledge of the physicochemical properties of pressurized substances, and their changes as a function of pressure and temperature, is necessary to mathematical modeling, design and control of the high-pressure technological processes. High-pressure methods are widely used during food manufacture, processing and conservation. High-pressure food processing is also applied to inactivate microorganisms. Contrary to the traditional methods, high-pressure food processing has very small influence on the sensorial and nutritional properties of pressurized food.

Presented in this paper method, can also be applied to investigate other liquids, e.g. fuels and biofuels, lubricants, polymers, etc.

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