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Investigation of High-Pressure Phase Transitions in Vegetable Oils by Measuring Phase Velocity of Longitudinal Ultrasonic Waves

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Abstract - **Monitoring and studying the pressure effect on liquid properties are becoming increasingly important in food, chemical, cosmetic and pharmaceutical industry as well as in laboratory practice. Accurate thermodynamic data in liquids as a function of pressure are required for studies the structure of liquids as well as for various engineering applications.**

Direct measurement of thermodynamic parameters is very difficult. The velocity of sound is related to many thermodynamic parameters and can be measured relatively simple.

In this work the variation of sound velocity and isothermal compressibility with hydrostatic pressure for triolein is evaluated up to 650 MPa. During the measurement we stated the phase transformation of triolein and the presence of the hysteresis of the dependence of sound velocity on pressure. To the authors' knowledge, the measurement of the sound velocity of liquids under high pressure during the phase transition is the novelty. From the performed measurements it results that the dependence of sound velocity on pressure can be used to investigate phase transformations in natural oils.

Keywords: Phase transitions, high pressure, longitudinal acoustic waves, phase velocity, compressibility

I. INTRODUCTION

High-pressure research of the physical properties of vegetable oils has been stimulated by the fast development of such technologies as high-pressure food processing and conservation as well as biodiesel production. High-pressure technologies (pressures up to 1 GPa) have proved a great potential in modern bioengineering as a method of modification of biotechnological materials [1]. High-pressure processing retains food quality, maintains natural freshness and extends microbiological shelf life inactivating micro-organisms. The knowledge of physical properties (e.g. compressibility, viscosity etc.) of treated substance is essential for understanding, design and control of the process technology. Measurement techniques for in-situ determining of physical parameters of liquids under high pressure allow insight into the phenomena governing the microstructural modifications.

Direct measurements of the physical properties such as density, compressibility and isobaric heat capacity are very difficult under conditions of very high-pressure. The speed of sound is closely linked with these thermodynamic properties and can be measured relatively easily and with high accuracy over wide ranges of temperature and pressure.

Most of the natural oils like castor oil, soybean oil, rapeseed oil, etc. consist of triglycerides of various fatty acids. The statistical characteristics of the molecular composition of these oils have made difficulties for the interpretation of the phenomena observed at high pressure. Therefore experiments have been concentrated upon well-

defined triacylglycerol (triglyceride) structures. A triglyceride and unsaturated fat – a triolein $(C_{17}H_{33}COO)C_3H_5$ has been selected as a model structure.

High-pressure phase transitions in liquids can be investigated e.g. by the measurement of the viscosity [2-4] or the acoustic wave phase velocity in function of hydrostatic pressure.

An understanding of the pressure dependence of sound speed, attenuation, and relaxation frequencies can provide valuable information as to transport quantities such as fluid viscosity and thermal conductivity along with ratios of specific heats [5-6]. Additionally, sound speed is closely related to derivatives of the equation of state. Therefore, the precision of these derivatives is often substantially better when they are deduce from the speed of sound rather than obtained from the analysis of classical pVT data.

In this study, we investigated the high-pressure behavior of triolein. Sound velocity and isothermal compressibility were measured in the pressure range up to 650 MPa. During the measurement, we stated the phase transformation of triolein and the presence of the hysteresis of the dependence of sound velocity on pressure.

II. MEASURING METHOD AND SETUP

For the measurements of the phase velocity of longitudinal ultrasonic waves the authors have constructed the setup (Fig.1) especially designed to obtain a low level of parasitic ultrasonic signals. A special mounting of transducers in the high-pressure chamber was fabricated. The transducers were 5 MHz $LiNbO_3$ (Y_{36} cut) plates (Boston Piezo-Optics Inc., USA). The phase velocity of the longitudinal ultrasonic wave was measured using a cross-correlation method to evaluate the time of flight (TOF).

High pressure was generated in a thick-walled cylinder with a simple piston and Bridgman II sealing system. The piston-cylinder assembly was working with a 20 ton hydraulic press, driven by a hand-operated pump. For pressure measurement 75 Ω manganin transducer was used. All experiments were carried out at the temperature 293 K.

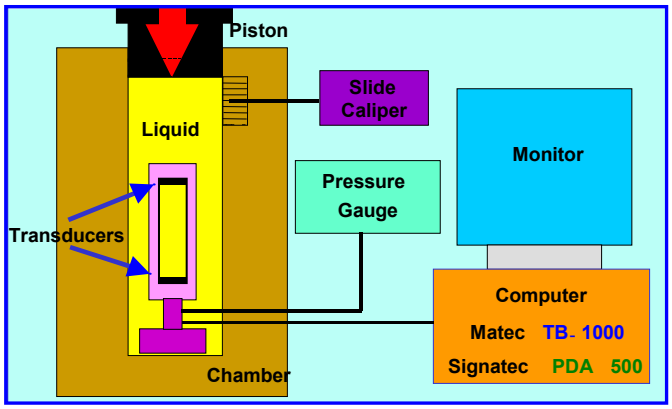

Fig.1. Ultrasonic setup for measuring the phase velocity of longitudinal acoustic waves in liquids as a function of hydrostatic pressure.

In the measuring setup, the sending transducer is driven by the TB-1000 pulser-receiver computer card (Matec, USA). The TB-1000 pulser generates the rf tone burst with a frequency 5 MHz and length equal to $0.3\,\mu s$. The longitudinal wave impulse generated by the sending transducer propagates in the investigated liquid and is detected by the receiving transducer. The PDA-500 digitizer card (Signatec, USA) samples and digitizes the signals received by the transducer and amplified by the TB-1000 receiver. The stored signals are 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 controls the operation of the pulser-receiver card and digitizer card was written in C language. The time of flight of the ultrasonic pulses was evaluated by applying the cross-correlation method. The cross-correlation method is a global differential method. Due to this reason, the cross-correlation method does not depend on the trigger level and delays in cables and amplifiers. The change in the height of column of liquid caused by the piston movement was measured by a digital caliper. The piezoelectric transducers and manganin coil were connected with the external measuring setup by an electrical multi-channel lead-through.

The sound velocity v_L was calculated using the formula:

$$v_L = \frac{l_0}{\Delta t} \qquad (1)$$

where: l_0 is the distance between sending and receiving transducer, Δt is time of flight (TOF) of the ultrasonic signal.

The isothermal compressibility β_T is given by the formula:

$$\beta_T = -\frac{1}{V}\frac{\partial V}{\partial p} \qquad (2)$$

where: V is the volume of a liquid in the measuring point, p is the hydrostatic pressure.

III. EXPERIMENTAL RESULTS

The measurements of the phase velocity (Fig.2) and isothermal compressibility (Fig.3) of triolein were carried out in function of hydrostatic pressure up to 650 MPa. The pressure was generated in 20 MPa steps then kept constant about 2 min. that allowed to control whether the system was reaching equilibrium. Up to 450 MPa the phase velocity was increasing monotonically with pressure (arrow 1 in Fig.2). After approaching 450 MPa the compression was stopped, and the piston in the high-pressure chamber was fixed to enable the phase transformation to occur undisturbed. During the phase transition a pressure drop of about 150 MPa was observed in the chamber. It means that the volume occupied by the resulting high-pressure phase of triolein diminished. The phase velocity showed the further rise despite the pressure drop (arrow 2 in Fig.2). Finally the phase velocity has risen to the new value characteristic for the high-pressure phase of triolein. Once the phase transition was completed the pressure was further increased up to about 650 MPa (arrow 3 in Fig.2). The phase velocity of longitudinal waves in high-pressure phase has increased monotonically. After approaching 650 MPa the decompression process was started (arrow 4 in Fig.2). At the point marked in Fig.2 by **a** the decomposition of the high-pressure phase started. Between points marked by **a** and **b** two phases coexisted in triolein.

The isothermal compressibility presented in Fig. 3 was calculated using Eq.2.

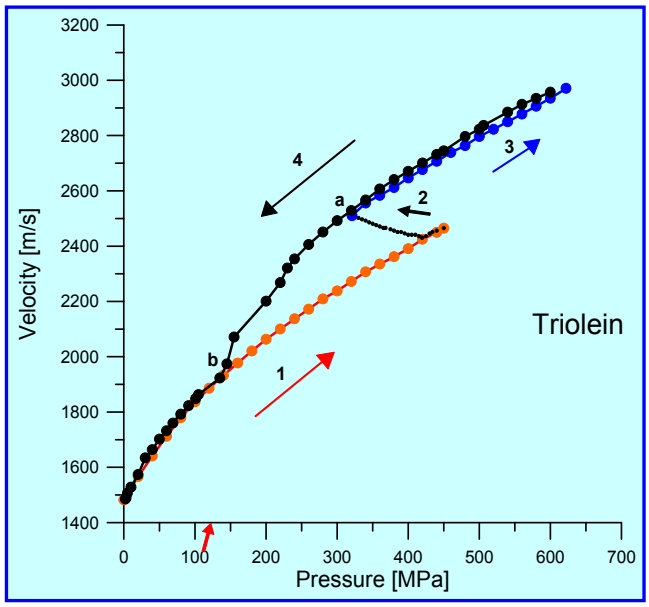

Fig.2. Phase velocity v_L of longitudinal acoustic waves in triolein in function of hydrostatic pressure. (1) refers to low-pressure phase, (2) indicates the phase transition, (3) refers to high-pressure phase, and (4) indicates the decompression. f = 5 MHz.

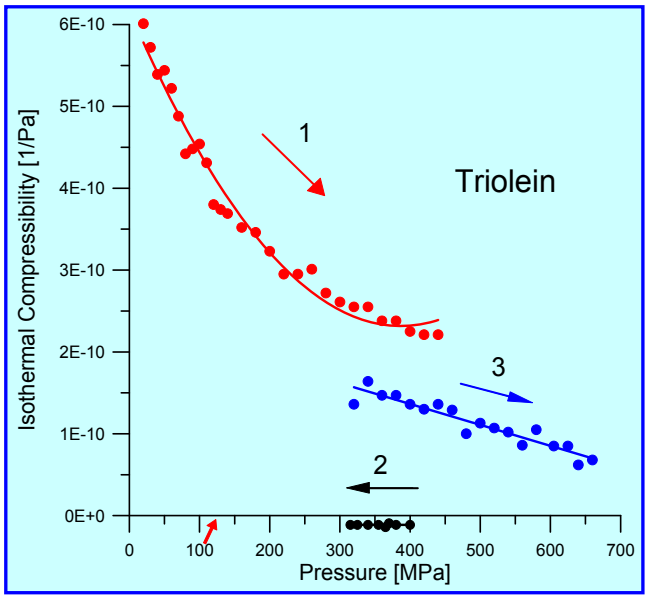

Fig.3. Isothermal compressibility of triolein β_T as a function of hydrostatic pressure. During the phase transformation (arrow 2) β_T is negative. f = 5 MHz.

The volume changes ΔV were determined from the changes of the height of the triolein column measured by the slide caliper. The arrows indicated by numbers 1, 2 and 3 in Fig.3 refer (similarly as in Fig.2) to the low-pressure phase, phase transition and high-pressure phase respectively.

It is worth noticing that the value of isothermal compressibility β_T during the phase transition is negative. Moreover, the isothermal compressibility of high-pressure phase is different than that of low-pressure phase.

IV. CONCLUSIONS

The results of measurements presented show:

1) Usefulness of constructed ultrasonic measuring setup for determining the sound velocity and compressibility of oils and other liquids at high pressure

2) Possibility of the measurement of the sound velocity during phase transitions and high-pressure phase decomposition

3) Low-pressure and high-pressure phases exhibit different values of the isothermal compressibility

4) Isothermal compressibility β_T during the phase transition is negative.

Measurement of the sound velocity of liquids under high pressure during the phase transition and during the decompression is an original authors contribution. To the authors knowledge such measurements were not reported in the scientific literature.

The proposed ultrasonic method can be computerized. This enables continuous (on-line) monitoring of the physical parameters of liquids, in-situ during the course of technological processes. Application of ultrasonic methods will provide real-time process monitoring and control thereby reducing down time and increasing product quality in food, chemical, cosmetic, pharmaceutical and petroleum industry.

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