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Determination of physicochemical properties of diacylglycerol oil at high pressure by means of ultrasonic methods

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A B S T R A C T

The purpose of the paper is to address, using ultrasonic methods, the impact of temperature and pressure on the physicochemical properties of liquids on the example of diacylglycerol (DAG) oil. The paper presents measurements of sound velocity, density and volume of DAG oil sample in the pressure range from atmospheric pressure up to 0.6 GPa and at temperatures ranging from 20 to 50 °C.

Sound speed measurements were performed in an ultrasonic setup with a DAG oil sample located in the high-pressure chamber. An ultrasonic method that uses cross-correlation method to determine the time-of-flight of the ultrasonic pulses through the liquid was employed to measure the sound velocity in DAG oil. This method is fast and reliable tool for measuring sound velocity. The DAG oil density at high pressure was determined from the monitoring of sample volume change. The adiabatic compressibility and isothermal compressibility have been calculated on the basis of experimental data. Discontinuities in isotherms of the sound speed versus pressure point to the existence of phase transitions in DAG oil. The ultrasonic method presented in this study can be applied to investigate the physicochemical parameters of other liquids not only edible oils.

1. Introduction

Development and design of products and processes for new industrial applications in chemical, food and petroleum industries require knowledge of the physicochemical properties of liquids as a function of temperature and pressure.

High-pressure research of the physicochemical properties of food products has been stimulated by the rapid development of a new technology of food processing, i.e., high-pressure food processing and preservation. To optimize the parameters of high -pressure technological processes (HPP), precise knowledge of the physicochemical parameters of food is indispensable. Unfortunately, there is a lack of physicochemical parameters of food under high-pressure conditions and for various values of temperature. Knowledge of high-pressure physicochemical properties of fuels and biofuels is also essential due to the increasing operating pressure in modern fuel injection systems.

Ultrasonic methods due to their simplicity and accuracy are the most commonly used in the investigation of liquids. Furthermore, the speed of sound is currently considered one of the most useful properties due to its relationship with certain physicochemical properties. Direct measurements of physicochemical properties are very difficult to carry out accurately. In this regard, measuring the speed of sound in liquids under high pressure, provides a relatively easy and accurate manner to obtain isothermal and adiabatic compressibility and other fundamental thermodynamic parameters of liquids.

The aim of this paper is to determine the high-pressure behavior of the physicochemical parameters (such as e.g., isothermal and adiabatic compressibility) of liquids on the example of diacylglycerol (DAG) oil. To this end, ultrasonic velocity and density measurements of DAG oil over the range of pressures and temperatures have been employed.

Diacylglycerol (DAG) is very ubiquitous fat in the food industry and as such is indispensable for good condition of all living organisms. Fat metabolism in the human body associated with the consumption of DAG is more efficient then the metabolism associated with triacylglycerides (TAG) [1–3]. Vegetable oils are currently important not only as foodstuffs but also as a basic ingredient of biofuels (i.e., biodiesels).

Understanding the thermodynamic and rheological properties of liquids is important for the researchers of food [4–10]. The sound velocity technique seems to be very convenient tool for

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the investigation of such properties of liquids. This knowledge can also be very useful in the petroleum industry and in the rapidly developing high-pressure food preservation industry.

Investigation of high-pressure phase transitions in liquids using existing until now classical methods (e.g., optical ones) is difficult. Therefore, for this purpose we applied the ultrasonic method and the measuring setup, that are very convenient to measure the sound velocity at high pressures [11,12]. Discontinuities in the measured isotherms of sound speed versus pressure in DAG oil, indicate the presence of liquid to solid-like phase transformations. Similar phase transitions were also observed in triglycerides and other edible oils [13–20].

On the basis of experimental results (speed of sound and density versus pressure and temperature), isotherms of adiabatic and isothermal compressibility of DAG oil were evaluated as a function of pressure. This work can be extended to other liquids, in order to investigate the temperature effect on their physicochemical properties under high pressure.

The results of this study can be applied in mathematical modeling and optimization of new technological methods of high-pressure food processing and preservation, as well as to model the new fuel injection systems in diesel or biodiesel engines.

According to the authors' best knowledge, the results presented in this paper are a novelty and have not been reported in the scientific literature.

2. Materials and methods

In this paper we measured the time of flight of the longitudinal ultrasonic wave between the transmitting transducer and receiving transducer. In this way, we have determined the speed of sound in the investigated DAG oil sample as a function of pressure for various temperatures. From the change in position of the piston in the high pressure chamber, sample volume changes were evaluated. On this basis, knowing the density of the sample measured by pycnometer at atmospheric pressure, we determined the changes in density of the sample as a function of pressure for various temperatures. Using the measured values of density and sound velocity, we determined changes in the isothermal compressibility and the adiabatic compressibility as a function of pressure for various values of temperatures employing analytical expressions specified in Section 3.

2.1. Sample

DAG oil sample was diacylglycerol oil that is composed of 82% of DAGs (57,4% of sn-1,3 and 24,6% of sn-1,2(2,3)) and 18% of TAGs [21]. The fractions were determined by means of the gas chromatography (GC) method using a Hewlett Packard HP6890 device. The analysis was conducted following the AOCS Cd 11b-91 method. The composition of fatty acid was obtained by the use of a Hewlett Packard HP 6890 device. The analysis was performed according to ISO 5508 and ISO 5509 norms, whereas the data were analyzed with ChemStation A 03.34 software.

2.2. Ultrasonic measurements

Velocity of sound in liquids in high-pressure condition and at various temperatures was measured in the cylindrical high-pressure chamber that constitutes an essential part of a computerized ultrasonic measuring setup, see Fig. 1.

The pressure inside the chamber was measured by the manganin resistive sensor. Ultrasonic pulses in the investigated sample were generated and received by means of piezoelectric transducers. The piezoelectric transducers were manufactured from $LiNbO_3$ (Lithium niobate Y36 cut) (Boston Piezo-Optics Inc., USA), with a diameter equal to 5 mm and 5 MHz fundamental frequency. The manganin sensor and the piezoelectric transducers (that have been placed inside the chamber) were connected to an external PC computer via a multi-channel electrical lead-through.

The high pressure chamber has a capacity of 22 cm^3. Computerized ultrasonic setup was designed and constructed in the Institute of Fundamental Technological Research, Polish Academy of Sciences. The pressure sensor was calibrated by means of a standard manometer with the measurement range up to 600 MPa [22,23]. The calibration process allows to measure pressure by means of resistance changes with accuracy of 0.1 MPa. T type thermocouple was used as a temperature sensor. The increase in pressurization was stopped whenever phase transitions had begun. After the phase transition termination, when thermodynamic properties were nearly at equilibrium (at high-pressure phase of DAG oil), pressurization was continued with the same compression rate as before.

The ultrasonic setup construction provides a low level of parasitic ultrasonic signals. The sending transducer was driven by the TB-1000 (Matec, USA) pulser–receiver computer card. The pulser generated the radio frequency one-cycle tone burst with a frequency of 5 MHz and a length 0.3 μs. The longitudinal wave pulse was generated by the sending transducer and propagated in the measured sample and subsequently was detected by the receiving transducer. The PDA-1000 (Signatec, USA) digitizer card sampled and digitized the signals received by the transducer and amplified by the receiver. For each measurement, the ultrasonic signal was averaged 1024 times in order to improve the signal-to-noise ratio. The time-of-light (TOF) is the time for the signal to travel from the sending transducer to the receiving transducer. The TOF of the ultrasonic pulses through the sample was evaluated by applying the cross-correlation method.

2.3. Ultrasonic wave velocity measurement by means of the cross-correlation method

The velocity c of ultrasonic waves propagating in a liquid along the path L is given by $c = L/t_d$: where: t_d is the TOF along the path L. The path length L is assumed to be a straight line, between two ultrasonic transducers (sending and receiving ones), immersed in a measured liquid and working in a through-transmission mode, Fig. 1. Since our measurements are always differential (time difference) all extra delays in cables, electronics, etc. will be cancelled. A measurement of the time difference between those two ultrasonic pulses and travel distance yields the sound speed in an investigated liquid.

Sound speed measurement is difficult and uncertain when using classical physical methods. To measure the TOF we employed the cross-correlation method [24,25] that improves considerably the accuracy of sound speed evaluation. The cross-correlation function $h(t)$, between two functions $f(t)$ and $g(t)$, is defined by Eq. (1):

$$h(t) = \int_{-\infty}^{+\infty} f(\tau)g(t+\tau)d\tau \tag{1}$$

The first received signal (the function $f(t)$) corresponds to the ultrasonic pulse, that passes the distance L between the transmitting and receiving transducers. Part of the ultrasonic energy of the first signal is reflected from the receiving transducer back to the transmitting transducer, which in turn reflects a part of the incident energy back to the receiving transducer. As a consequence, the next pulse detected by the receiving transducer (function $g(t)$) will pass an extra distance $2L$ between the transducers. In total, this signal passes the distance $3L$. The analysis of correlation

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