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Employment of a novel ultrasonic method to investigate high pressure phase transitions in oleic acid

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In this work, the variation of sound velocity with hydrostatic pressure for oleic acid is evaluated up to 350 MPa. During the measurement, we identified the phase transformation of oleic acid and the presence of the hysteresis of the dependence of sound velocity on pressure. From the performed measurements, it can be seen that the dependence of sound velocity on pressure can be used to investigate phase transformations in natural oils. Ultrasonic waves were excited and detected using piezoelectric LiNbO₃(Y-36 cut) 5 MHz transducers. The phase velocity of the longitudinal ultrasonic waves was measured using a cross-correlation method to evaluate the time of flight.

Keywords: sound velocity; oleic acid; high pressure; phase transition

1. Introduction

Studies of the physical properties of oliferous liquids have been stimulated by the fast development of the food, chemical and textile industries. Understanding of the thermodynamic properties of liquids and also their transport properties is very important for these technologies. The measurement of sound velocity appears to be a very useful tool for the investigation of such properties. Especially at high pressure conditions, ultrasonic parameters such as sound velocity and absorption of acoustic signals enable us to calculate important parameters such as fluid viscosity, thermal conductivity and adiabatic compressibility.

Sound propagation is unique in that it is an adiabatic process: thus, sound speed data give direct and precise information about the adiabatic properties of a liquid. Additionally, sound speed is closely related to derivatives of the equation of state [1,2]. 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. The sound velocity dependence on temperature

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as well as on pressure can be a source of valuable information about phase transitions in an investigated material [3–5].

After successful application of ultrasonic methods for the viscosity measurement at high pressure conditions using surface waves (Bleustein-Gulyaev and Love waves) [6,7], we have developed a method of sound velocity measurement based on our experience from such experiments. The first measurements of sound velocity under pressure using this method were done in triolein within a pressure range up to 650 MPa [8]. In these experiments, the changes of sound velocity during the first-order phase transition were observed. In the present paper, oleic acid, another member of the large group of organic compounds called lipids, was investigated within a range up to 350 MPa.

2. Properties of oleic acid

High pressure research of the physical properties of lipids has been stimulated by the fast development of technologies such as high pressure food processing and conservation, as well as biodiesel production. The statistical characteristics of the molecular composition of these oils have caused difficulties for the interpretation of the phenomena observed at high pressures. Therefore, experiments have been concentrated upon well-defined triacylglycerol (triglyceride) structures and also on liquids with acyl chains. As a model structure representing triglycerides, a triolein ($C_{17}H_{33}COO$) C_3H_5 has been selected, whereas for a material representing mechanical properties of single acyl chains, pure free oleic acid ($C_{18}H_{34}O_2$) has been used [9,10]. Oleic acid at low temperatures can crystallize in one of three polymorphic forms: α , β or γ [11].

The first experiments on high pressure properties of oleic acid are described in [12]. They have shown the existence of a first-order phase transition at pressures of about 200 MPa.

Further experiments on X-ray diffraction under pressure [13] have proved that the discovered phase transition is a liquid to β -crystal form transition. The aim of the present experiments is to learn more about the properties of both the liquid and solid phases.

3. Experiments

Measurements were performed in a setup (Figure 1) designed and constructed by us. High pressure was generated in a thick-walled cylinder with a simple piston and Bridgman II sealing system. The piston–cylinder assembly works with a 20 ton hydraulic press, driven by a hand-operated pump. For pressure measurements, a 75 Ω manganin transducer was used. All experiments were carried out at the temperature of 293 K.

The piezoelectric transducers and manganin coil were connected to the external measuring setup by an electrical multi-channel lead-through.

The accuracy of the measurements of ultrasonic wave-phase velocity depends on the level of parasitic ultrasonic signals. Therefore, we designed a special mounting of ultrasonic transducers in the high pressure chamber. This construction produces a low level of parasitic ultrasonic signals. Longitudinal ultrasonic waves were excited and detected using 5 MHz LiNbO₃ (Y₃₆ cut) plates (Boston Piezo-Optics Inc., USA).

The sending transducer was driven by the TB-1000 pulser–receiver computer card (Matec, USA). The pulser generated the radio frequency (rf) tone burst with a frequency of 5 MHz and a length 0.3 μ s. The longitudinal wave pulse was generated by the sending transducer propagated in the oleic acid and was detected by the receiving transducer. The PDA-1000 digitizer card (Signatec, USA) sampled and digitized the signals received by the transducer and amplified by the receiver. The stored signals were then analyzed by computer software. For each measurement,

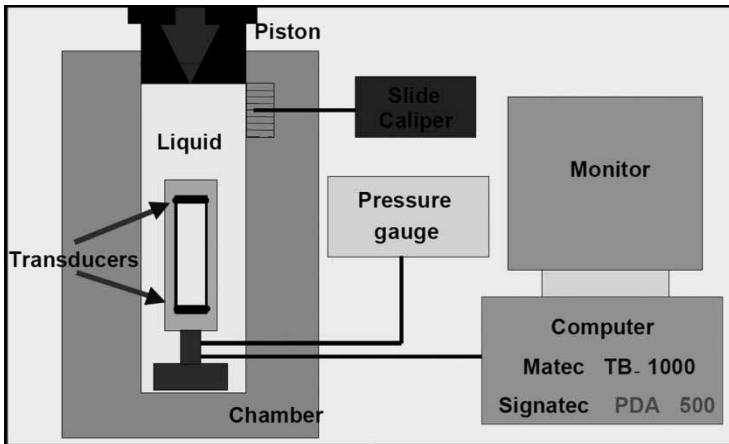


Figure 1. Ultrasonic setup for measuring the phase velocity of longitudinal acoustic waves in liquids as a function of hydrostatic pressure. The ultrasonic transducers are separated by a distance L .

the ultrasonic signal was averaged 1024 times in order to improve the signal-to-noise ratio. The computer program that controls the operation of the pulser–receiver card and digitizer card was written in C++ language. The time-of-flight (TOF) of the ultrasonic pulses was evaluated by applying the cross-correlation method.

3.1. Measurement of ultrasonic wave velocity in liquids using the cross-correlation method

The velocity c of ultrasonic waves propagating in a liquid along a path L is given by

$$c = \frac{L}{t_d}, \quad (1)$$

where t_d is the TOF along 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 (Figure 1). In practice, we always observe a number of ultrasonic impulses, multiply reflected between two ultrasonic transducers facing each other. In the experimental arrangement shown in Figure 1, the first impulse received by transducer travels the path L through an investigated liquid. The next impulse will travel the path $3L$, etc. To determine the speed of sound, we select two ultrasonic impulses: first, one that passes the distance L , and second, one that passes the distance $3L$. 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 of the investigated liquid.

The ultrasonic velocity measurement is difficult and uncertain when calculated using classical methods. Instead, it is possible to use methods based on digital signal processing, such as the cross-correlation function [14–16]. The cross-correlation function $h(t)$ between two functions, $f(t)$ and $g(t)$, is defined by Equation (2):

$$h(t) = \int_{-\infty}^{\infty} f(\tau)g(t + \tau)d\tau. \quad (2)$$

The first received signal (the function $f(t)$) corresponds to the ultrasound pulse that passes the distance L between the transmitting and receiving transducers. Part of the ultrasonic energy of the

first signal is reflected at the receiving transducer back to the transmitting transducer, which in turn reflects part of the incident energy back to the receiving transducer. As a result, the next impulse detected by the receiving transducer (function $g(t)$) will travel an extra $2L$ distance between the transducers. In total, this signal passes the distance $3L$.

The correlation analysis yields a measure of the similarity between the two considered pulses $f(t)$ and $g(t)$ shifted in time. Because these two pulses have similar shape but different amplitudes and delays, the cross-correlation function reaches a maximum for t equal to the evaluated time difference corresponding to the distance $2L$.

The time delay was measured with a nanosecond resolution. The relative uncertainty for the ultrasonic velocity in liquid equals $\pm 0.3\%$ at a 95% confidence level.

4. Results

The measurements of the phase velocity (Figure 2) of oleic acid were carried out as a function of hydrostatic pressure up to 350 MPa. The pressure was generated in 10 MPa steps and then kept constant for about 2 min, which allowed us to monitor whether the system was reaching equilibrium.

Up to 200 MPa, the phase velocity increased monotonically with pressure. After approaching 200 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 was observed in the chamber. This meant that the volume occupied by the resulting high pressure phase of triolein diminished. The phase velocity showed a further rise despite the pressure drop. Finally, the phase velocity rose to the new value, characteristic of the high pressure phase of oleic acid. Once the phase transition was complete, the pressure was further increased up to about 350 MPa. The phase velocity of the longitudinal waves in the high pressure phase increased monotonically. After approaching 350 MPa, the decompression process was started. At a pressure of about 170 MPa, the decomposition of the high pressure phase started. Between the pressures of 170 and about 40 MPa, the two phases coexisted in the oleic acid.

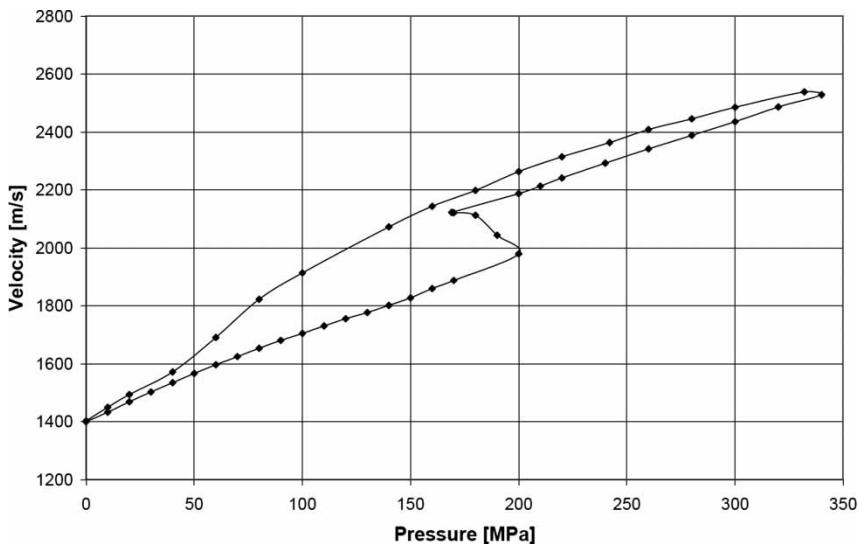


Figure 2. Phase velocity c of longitudinal acoustic waves in oleic acid as a function of hydrostatic pressure, $f = 5$ MHz.

5. Conclusions

The presented results of the measurements show:

- (1) the usefulness of the constructed ultrasonic measuring setup for determining the sound velocity of fatty acids and natural oils at high pressure;
- (2) the possibility of the measurement of sound velocity during phase transitions and high pressure phase decomposition;
- (3) that the dependence of sound velocity on pressure can be used to investigate phase transitions in natural oils.

Measurement of the sound velocity of liquids under high pressure during the phase transition and during decompression is the first contribution of its kind. To the best of our knowledge, such measurements have not been reported before in scientific literature.

The presented measuring method uses a cross-correlation method and is a global differential method. Due to this reason, this measuring method does not depend on the trigger level or delays in cables and amplifiers.

The proposed ultrasonic method can be computerized. This enables continuous (online) 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 downtime and increasing product quality in the food, chemical, cosmetic, pharmaceutical and petroleum industries.

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