



# Application of ultrasonic wave celerity measurement for evaluation of physicochemical properties of olive oil at high pressure and various temperatures



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## ABSTRACT

High-pressure processing is a powerful technology for food preservation. The knowledge of foods properties in the high-pressure range is important to develop and optimize such processes by means of mathematical modeling and simulation. Ultrasonic methods are rapid, non-invasive and can be used to characterize foods like edible oils (e.g., composition, purity, and quality assessment). In this paper, they were applied for the investigation of physicochemical properties of olive oil at high pressure at different temperatures. The sound wave velocity was measured by the pulse-transmission method and the corresponding oil density was additionally determined from the monitoring of sample volume change. Measurements were conducted in the pressure range up to 600 MPa, for temperatures from 20 to 50 °C. Intermolecular free length, isothermal and adiabatic compressibility versus pressure were calculated using measured sound speed and density isotherms. Discontinuities in the measured isotherms of sound speed and density versus pressure indicate the presence of liquid-to-solid phase transitions. The kinetics of the liquid-to-solid phase transition was also investigated. The transformation times of olive oil augment with increasing temperature. This study can be broadened to other liquid foodstuffs to investigate the influence of temperature on their physicochemical properties at high pressure.

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## 1. Introduction

Edible oils are an important constituent of human diet because they provide desirable nutritional properties, flavor and texture of food. Olive oil is one of the most frequently used edible oils. Therefore knowledge of its physicochemical properties is indispensable. Ultrasonic methods are very valuable tool for their evaluation. These methods are nondestructive and can be applied for on-line monitoring of technological processes in food industry (Bamberger & Greenwood, 2004; Hægström & Luukkala, 2000; Saggin & Coupland, 2001; Scanlon, 2004). Investigation of ultrasonic waves and their propagation, and its potential applications in food science and technology is still not well recognized.

Ultrasonic methods can also be used for investigations of high-pressure phase transitions (Kiełczyński et al., 2012). This is very important because high-pressure methods are often used during

food manufacture, processing and conservation (Kadam, Jadhav, Salve, & Machewad, 2012; Rastogi, Raghavarao, Balasubramaniam, Niranjana, & Knorr, 2007). Phase transitions that occur during the pressurization of oils are accompanied by serious changes of the physicochemical and mechanical properties (Indrawati, Van Loey, & Hendricx, 2002; LeBail et al., 2003). Measurement techniques for *in-situ* determining of physicochemical parameters of liquid foodstuffs under high pressure allow insight into the phenomena governing the microstructural modifications.

Knowledge of key physicochemical properties (e.g., density, compressibility) of pressurized substances is essential for understanding, design and control of the process technology. Physicochemical data are available in literature for foods at atmospheric pressure, but they are scarce for high-pressure range (Kowalczyk et al., 2005). The unavailability of physicochemical properties of food as a function of pressure is an important problem for teams working on high-pressure food processing modeling and optimization (Guignon, Aparicio, & Sanz, 2009).

Ultrasonic methods can also be used to measure the viscosity of oils (Kiełczyński, Szalewski, Balcerzak, Rostocki, & Tefelski, 2011;

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Kietczyński, Szalewski, Siegoczyński, & Rostocki, 2008; Rostocki, Siegoczyński, Kietczyński, & Szalewski, 2010). Viscosity measurement is an important component of many quality control and process monitoring procedures in food processing (Cullen, Duffy, O'Donnell, & O'Callaghan, 2000).

Measurements of sound speed in oils can be used to evaluate their physicochemical properties and to investigate high-pressure phase transitions (Koc & Vatandas, 2006; McClements, 1997; Rostocki et al., 2011; Sankarappa, Kumar, & Ahmad, 2005). Employing the results of the sound speed measurements in edible oils and other food products, it is possible to control their quality (Aouzale, Chitnalah, & Jakjoud, 2010; Awad, Moharram, Shaltout, Asker, & Youssef, 2012) and to evaluate frying oil degradation (Benedito, Garcia-Pérez, Dobarganes, & Mulet, 2007).

Publications concerning the development of *in-situ* measurement techniques under high pressure are very scarce in the food science literature. Existing until now, classical methods of measuring thermodynamic properties are very difficult to apply at high-pressure conditions. An alternative approach, a non-invasive technique, inherently capable of yielding high accuracy, is to measure compressibility/density and their pressure dependence by using acoustic methods (Van Dael & Van Itterbeek, 1965).

In our previous paper (Rostocki et al., 2013), the authors on the basis of measurements of the longitudinal ultrasonic wave velocity and density determined adiabatic compressibility as a function of hydrostatic pressure. Measurements were carried out at ambient temperature only. The current work is an extension of the above-mentioned paper published in JAOCS.

The objective of the study is to address the influence of temperature on the physicochemical properties of olive oil under high-pressure conditions, by means of ultrasonic speed and density measurements. Moreover, some new complementary thermodynamic parameters such as intermolecular free path lengths were determined. Temperature has a large impact on the kinetics of phase transformation and the values of physicochemical parameters of olive oil.

The speed of sound is linked to adiabatic compressibility and density. Therefore, a number of thermodynamic functions can be derived by measuring the speed of sound over a range of pressures and temperatures (Barbosa, 2003). We have also investigated kinetics of high-pressure liquid-to-solid phase transition in olive oil at various temperatures. This kind of phase transitions is responsible for crystallization of vegetable oils (Tarakowski, Malanowski, Kościeszka, & Siegoczyński, 2014).

Measurements of the longitudinal acoustic wave phase velocity and olive oil density were performed in the pressure range from atmospheric pressure to 600 MPa and at temperatures  $T = 20, 30, 40,$  and  $50\text{ }^{\circ}\text{C}$ .

Based on the measured sound speed and density, isotherms of adiabatic compressibility, intermolecular free length, and isothermal compressibility as a function of pressure were evaluated. Knowledge of compressibility and density changes as a function of pressure is very important in the processes of the high-pressure food processing and preservation (Min, Sastry, & Balasubramaniam, 2010).

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

### 2.1. Materials

For our experiments we used olive oil produced in Spain. Its chemical composition was evaluated by means of the gas chromatography method using Hewlett–Packard HP 6890 device with Flame Ionization Detector and high-polar column BPX70. The analysis was conducted following the AOCs Cd 11b-91 method and was performed according to the ISO 5508 and ISO 5509 norms. Composition of the investigated olive oil is presented in Table 1. There are five major fatty acids: the dominant C18:1*cis* oleic acid, C16:0 palmitic acid, C18:2 *cis*–*cis* linoleic acid, C18:0 stearic acid and C16:1 palmitoleic acid. Other fatty acids are presented in small amounts below 1%. This information may allow the comparison of our results with those obtained for olive oils of similar compositions. Olive oils that differ in composition and thus in their properties depending on the cultivar, the soil, the extraction process, etc. (Bonnet, Devesevre, Artaud, & Moulin, 2011). The volume of the investigated olive oil sample was  $22\text{ cm}^3$ .

### 2.2. Measuring setup

High-pressure measurements of the small signal sound speed were performed using the setup designed and constructed by the authors, see Fig. 1. High pressure was generated in a thick-walled cylinder chamber (length = 23 cm, diameter = 1.7 cm, capacity =  $52\text{ cm}^3$ ) with a simple piston and Bridgman II sealing system. Pressure was applied by a manually driven hydraulic press. Volume changes were measured by observation of piston displacement in the chamber. The piston displacement was measured by a digital caliper gauge, with an accuracy of 0.01 mm. The pressure inside the chamber was measured by a  $100\ \Omega$  manganin sensor calibrated using a dead weight piston gauge with a relative uncertainty of 0.05% (Rostocki, Urbański, Wiśniewski, & Wilczyńska, 2005). The manganin sensor resistance was measured using a linear unbalanced resistance bridge (Rostocki & Wiśniewski, 1977). Constant temperature in the chamber ( $\pm 0.1\text{ }^{\circ}\text{C}$ ) was maintained by a thermostatic water bath and a precision thermostat (Julabo Labortechnik, Germany). A copper–constantan thermocouple was placed inside the high-pressure chamber.

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 (Kietczyński, Szalewski, Rostocki, Zduński, & Balcerzak, 2009; Rostocki et al., 2011). A special mounting of transducers in the high-pressure chamber was fabricated. The piezoelectric transducers were  $\text{LiNbO}_3$  (Lithium niobate Y36 cut) plates (Boston Piezo-Optics Inc., USA), with diameter equals 5 mm and resonant frequency  $f = 5\text{ MHz}$ .

In the measuring setup, the sending transducer is driven by the TB-1000 pulser-receiver computer card (Matec, USA). The TB-1000 pulser generates RF tone burst signal with a frequency of 5 MHz, with a length equal to  $0.3\ \mu\text{s}$  and repetition time = 0.8 ms. The ultrasonic impulse generated by the transmitting transducer propagates in the investigated olive oil sample and is detected by

**Table 1**

Composition of investigated olive oil evaluated by means of the gas chromatography method. *c* and *t* stand for *cis* and *trans* configurations, respectively.

fatty acid	C14:0	C16:0	C16:1	C17:0	C17:1	C18:0	C18:1 <i>c</i>	C18:2 <i>ct/tc</i>
% in olive oil	<0.1	11.02	1.01	0.1	0.1	3.4	76.8	<0.1
fatty acid	C18:2 <i>cc</i>	C18:3 <i>ccc</i>	C20:0	C20:1	C20:2	C22:0	C24:0	C24:1
% in olive oil	5.9	0.7	0.4	0.3	<0.1	0.1	<0.1	<0.1

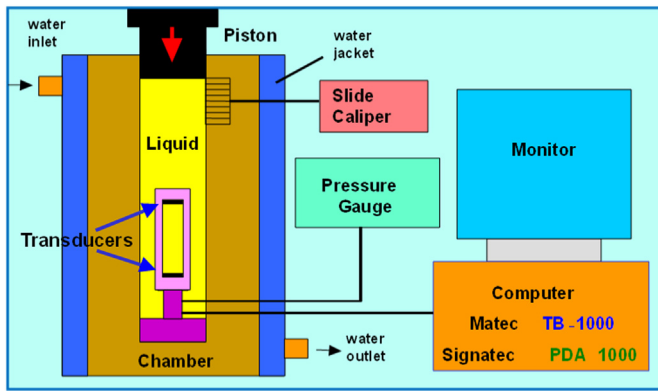


Fig. 1. Experimental ultrasonic setup for measuring the sound velocity in liquids at high pressure and various values of temperature (Kielczyński et al., 2009).

the receiving transducer. The PDA-1000 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 measurements, 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 density was measured at atmospheric pressure (at various temperatures), using a U-shaped tube densitometer (MG-2 UniLab, Poland). Since the mass of the sample did not change during the experiment, changes in volume can be used to determine the density changes as a function of pressure. Volume change was evaluated by measuring the displacement of the piston in the chamber, by means of a digital caliper.

The pressure was generated in 10 MPa steps, then kept constant for about 5 min. During that time the pressure and temperatures were observed. That allows the detection of the pressure drop due to phase transition and the observation whether the system was reaching thermodynamic equilibrium.

### 2.3. Measurement of ultrasonic wave velocity in liquids using 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 time-of-flight (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. In practice, we always observe a number of ultrasonic impulses, repeatedly reflected between two ultrasonic transducers facing each other. 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 subsequent ultrasonic impulses. Since our measurements are differential (time difference), 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. Application of digital signal processing methods to determine the time-of-flight of two subsequent ultrasonic pulses, improves considerably the accuracy of sound speed evaluation. To measure the time-of-flight we employed the cross-correlation method (Sugasawa, 2002; Viola & Walker, 2003). The analysis of correlation provides a measure of similarity between the two considered pulses  $f(t)$  and  $g(t)$  shifted in time. Since these two

pulses are of similar shape but different amplitude and delay, the cross-correlation function reaches its maximum at  $t$  equal to the evaluated time difference corresponding to the distance  $2L$ . The time delay was measured with uncertainty  $\pm 1$  ns.

The distance between the transducers was determined from the calibration measurements in water as the reference liquid. Knowing, with high accuracy the speed of sound in water at a given temperature (NIST data) and measuring the time-of-flight, the distance between the transducers was calculated. At ambient temperature, the distance  $L = 10.278$  mm. Distance  $L$  was evaluated with the uncertainty of  $\pm 10$   $\mu\text{m}$ .

### 2.4. Uncertainty analysis

According to the ISO guidelines (BIPM & ISO, 1995) the expanded relative uncertainty of the ultrasonic velocity  $\Delta U_c/U_c$ , can be expressed as

$$\frac{\Delta U_c}{U_c} = 2\sqrt{\left(\frac{\Delta U_L}{U_L}\right)^2 + \left(\frac{\Delta U_{t_d}}{U_{t_d}}\right)^2} \quad (1)$$

where:  $\Delta U_L/U_L$  is the relative standard uncertainty of the path  $L$ ,  $\Delta U_{t_d}/U_{t_d}$  is the relative standard uncertainty of the TOF delay  $t_d$ .

The time delay was measured with a picoseconds resolution. However, due to extra systematic errors, such as diffraction contribution, etc., the resulting relative standard uncertainty  $\Delta U_{t_d}/U_{t_d}$  for the TOF delay  $t_d$  was estimated as:  $\Delta U_{t_d}/U_{t_d} = \pm 0.1\%$ . Similarly, the relative standard uncertainty of the path  $L$  (resulting from calibration measurements in water) was estimated as:  $\Delta U_L/U_L = \pm 0.1\%$ . Consequently, the expanded relative uncertainty for the sound speed in liquid equals  $\pm 0.3\%$  at a 95% confidence level.

## 3. Results

### 3.1. Measurements results

#### 3.1.1. Sound speed

The plots of measured longitudinal ultrasonic wave velocity  $c$  in the investigated edible oil (olive oil) as a function of pressure, at

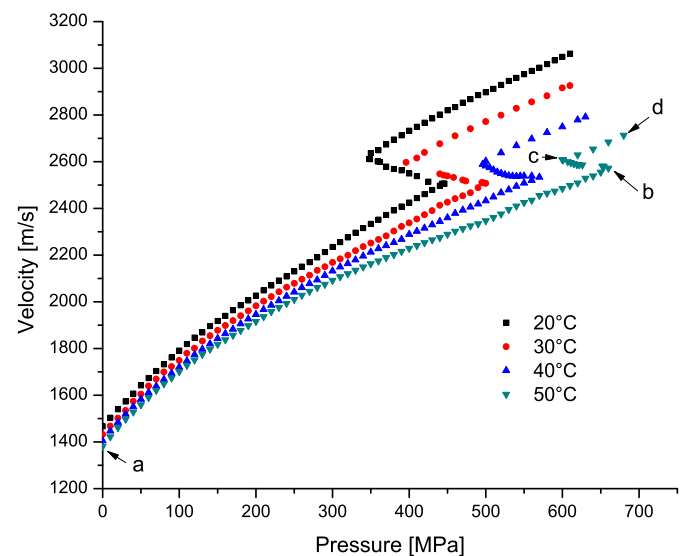


Fig. 2. Plots of sound velocity in olive oil as a function of pressure along various isotherms ( $T = 20, 30, 40,$  and  $50$  °C). From point a to point b, low-pressure phase of olive oil is observed. At point b phase transition begins. Point c indicates the termination of phase transition. From point c to point d, high-pressure phase of olive oil occurs,  $f = 5$  MHz.

various temperatures, are shown in Fig. 2. The plot of sound speed (see Fig. 2) displays a piecewise monotonically continuous character of  $c$  as a function of pressure for various values of temperature. The increase in ultrasonic speed is due to the decrease in intermolecular free path length and adiabatic compressibility. Discontinuity in the plot indicates that the phase transition occurs. In Fig. 2, three different parts of each curve can be seen. At the beginning of measuring process (point  $a$ ), the pressure was increased gradually up to the point  $b$ , (first part of each curve in Fig. 2). At the moment corresponding to point  $b$ , we stopped the compression, and the piston in the high-pressure chamber was fixed to enable the liquid-to-solid phase transition to occur undisturbed. The induction time is the time that elapses from the moment when the piston is stopped and the beginning of the phase transformation (marked by spontaneous pressure drop associated with transition). The observed spontaneous pressure drop indicates initiation of the liquid-to-solid phase transition. The pressure drop is due to a decrease in the liquid volume, and consequently the increase in the liquid density. These changes result from the phase transition that occurs spontaneously. Although the pressure drops, the speed of sound continues to increase (second part of each curve in Fig. 2). This indicates change in the physical properties of the liquid.

When the temperature during measurements was higher, the pressure, at which the liquid-to-solid phase transition began, increased. The stabilization of pressure and negligible changes in sound velocity indicated that the liquid-to-solid phase transition was completed (point  $c$ ). At the termination of the phase transition process the pressure was increased again, in order to measure the sound velocity in the new high-pressure solid-like phase of olive oil (third part of each curve in Fig. 2). The further increase of velocity with increasing pressure was observed (up to point  $d$ ).

### 3.1.2. Kinetics of phase transition

The kinetics of the liquid-to-solid phase transition was investigated during sound speed measurements, see Fig. 3. Pressure changes, occurring during liquid-to-solid phase transition, were registered with the piston locked in a fixed position. At first (starting at the point  $b$  at a given temperature) the pressure remained constant. Subsequently, a sudden decrease of pressure was observed (at point  $b_1$ ), due to a liquid-to-solid phase transition

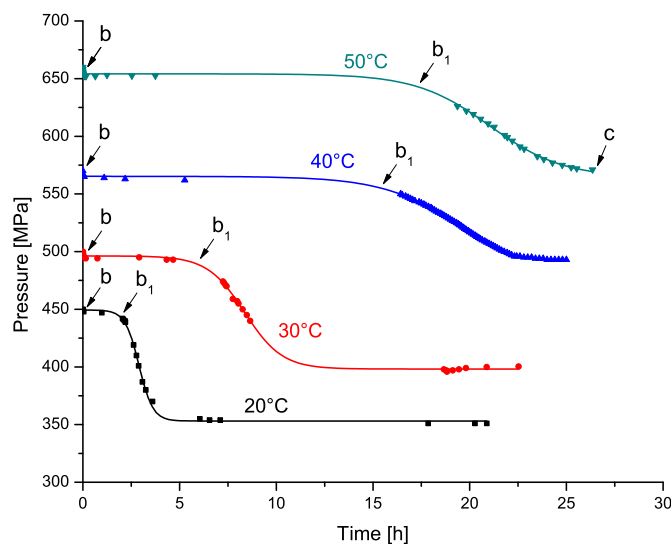


Fig. 3. Kinetics of phase transition in olive oil at various temperatures ( $T = 20, 30, 40$ , and  $50^\circ\text{C}$ ). Points  $b$  and  $c$  refer to the corresponding points  $b$  and  $c$  in Fig. 2. Point  $b_1$  indicates the beginning of a phase transition.

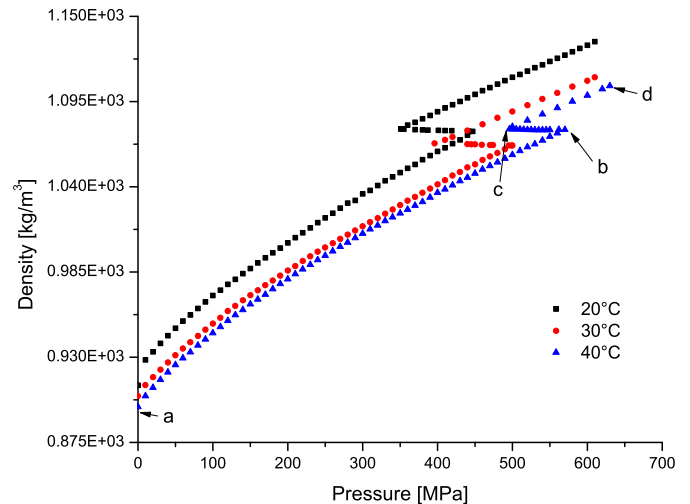


Fig. 4. Variation of olive oil density versus pressure at temperatures: ( $T = 20, 30$ , and  $40^\circ\text{C}$ ). Points  $a$  and  $b$  delimit low-pressure phase region. Points  $b$  and  $c$  designate phase transition region. Points  $c$  and  $d$  determine high-pressure phase region.

in olive oil. The moment of time in which, pressure drops spontaneously with further increase in the speed of sound is the signature of the beginning of the phase transition. Finally, the pressure level stabilized (point  $c$ ). This means that the liquid-to-solid phase transition was completed. As a result, a new high-pressure solid-like phase in olive oil has emerged. Changes in temperature influence considerably the time course (evolution) of phase transition. One can see in Fig. 3, that with the increase of temperature liquid-to-solid phase transition started at a higher value of pressure and the induction time (from point  $b$  to point  $b_1$ ) is larger.

### 3.1.3. Density

During experiments, olive 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 olive oil density as a function of pressure, for various temperatures, see Fig. 4. The olive oil density shows a piecewise monotonically continuous behavior of  $\rho$  versus the pressure for various values of temperature. Discontinuity in the curve indicates that the liquid-to-solid phase transition occurs.

## 3.2. Calculation results

Measured values of sound velocity and density in olive oil versus pressure have been used to calculate intermolecular free length, isothermal compressibility, and adiabatic compressibility as a function of pressure.

### 3.2.1. Intermolecular free length

The intermolecular free length has a clear physical significance i.e., it is the distance between the surfaces of the neighboring molecules and is related to ultrasonic velocity and density as follows (Kavitha, Jayakumar, Kannappan, & Uma, 2013):

$$L_f = K/c(\rho)^{1/2} \quad (2)$$

where:  $\rho$ , density;  $c$ , sound velocity;  $K$  is the Jacobson's constant given by the relation:  $K = (93.875 + 0.345 \cdot T) \cdot 10^{-8}$ ; and  $T$  is temperature in K.

Changes in the molecular structure of olive oil constituents alter the intermolecular free path length (Banu & Prasad, 2013). Fig. 5 presents the plot of isotherms of intermolecular free length versus pressure. Discontinuities observed in curves in Fig. 5 can be a signature of phase transition.

### 3.2.2. Isothermal compressibility

Isothermal compressibility was evaluated using the relation

$$\beta_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \quad (3)$$

where  $V$  is volume and  $p$  is pressure.

The derivative in Eq. (3) was calculated numerically.

Fig. 6 shows isothermal compressibility evaluated with Eq. (3) as a function of pressure at  $T = 20^\circ\text{C}$ . Due to the presence of liquid-to-solid phase transition the curve in Fig. 6 is discontinuous. Isothermal compressibility of the high-pressure phase is lower than that in the case of the low-pressure phase. This shows that the high-pressure phase exhibit properties similar to a solid-like medium. The spread of points in Fig. 6 results from the numerical evaluation of the derivative in Eq. (3). The solid line is an approximation of the computed points of isothermal compressibility. Numerical calculations of the derivative are always accompanied by errors. This leads to the spreading of points in Fig. 6.

### 3.2.3. Adiabatic compressibility

Adiabatic compressibility of olive oil (see Fig. 7) was calculated using the equation

$$\beta_s = \frac{1}{\rho \cdot c^2} \quad (4)$$

Compressibility of a liquid is one of the important physical quantities in fluid mechanics. It depends on the structure of the liquid. Compressibility is determined by the balance between attractive and repulsive forces and enters into many pressure dependent thermodynamics expressions. It decreases with pressure augmentation because free volume between molecules decreases (Min et al., 2010). Compressibility is a key property of foods during high-pressure processing (Barbosa, 2003). As it can be

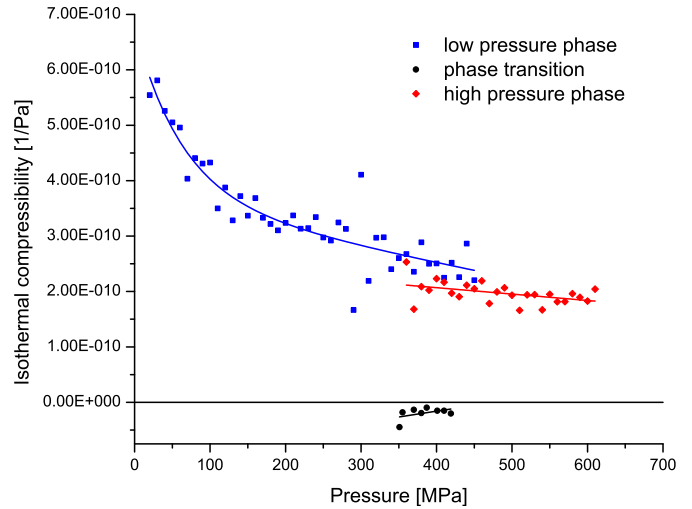


Fig. 6. Isothermal compressibility of olive oil as a function of pressure at  $T = 20^\circ\text{C}$ . Discrete points were evaluated using Eq. (3). Solid line is an approximation curve of the calculated discrete data. The discontinuity in the solid curve indicates the liquid-to-solid phase transition.

seen in Fig. 7, isotherms of adiabatic compressibility exhibit discontinuity, what indicates the presence of phase transition.

Increase in temperature results in an increase of intermolecular distance. Therefore, the liquid becomes less packed, and hence the intermolecular free length and adiabatic compressibility increase, and consequently the density and ultrasonic longitudinal phase velocity decrease, see Figs. 2, 4, 5 and 7. Adiabatic compressibility of the high-pressure phase is lower than adiabatic compressibility for low-pressure phase.

## 4. Discussion

Monotonic decrease in the specific volume of olive oil, with the pressure rise has been observed in the works: Acosta, Smith, and Arai (1996), Guignon et al. (2009). This corresponds to the increase in the density of olive oil (Werner, Baars, Eder, & Delgado, 2008). The density of olive oil measured by the authors displays the same trend: i.e., the density increased, when the pressure was

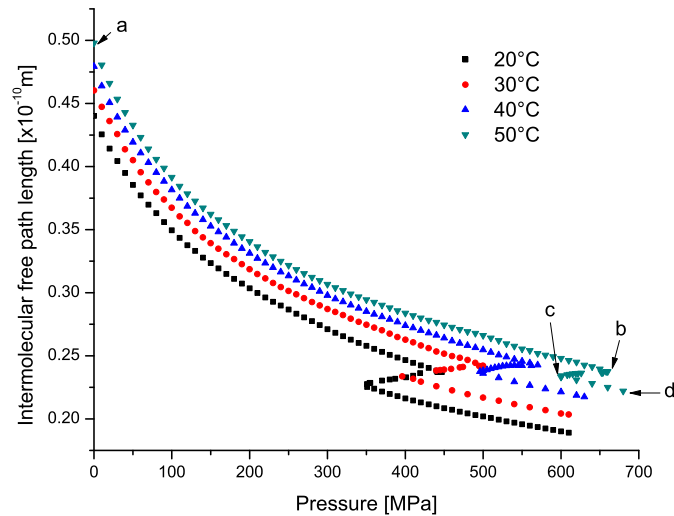


Fig. 5. Intermolecular free length isotherms versus pressure ( $T = 20, 30, 40,$  and  $50^\circ\text{C}$ ) in olive oil. From point  $a$  to point  $b$ , low-pressure phase of olive oil is observed. At point  $b$  phase transition begins. Point  $c$  indicates the termination of phase transition. From point  $c$  to point  $d$ , high-pressure phase of olive oil occurs.

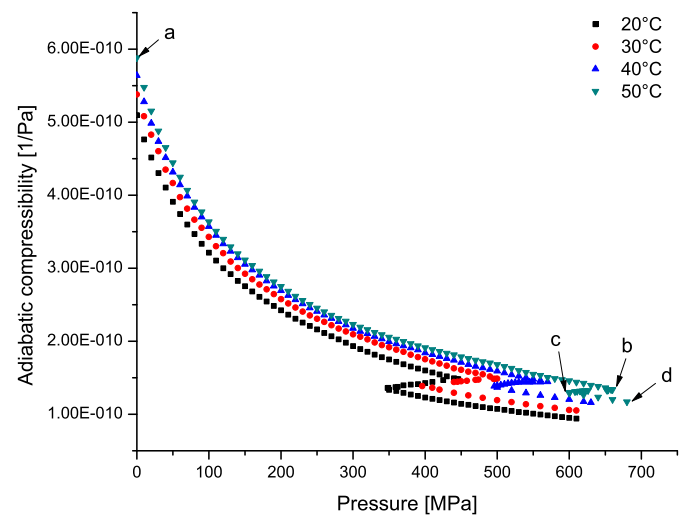


Fig. 7. Adiabatic compressibility of olive oil isotherms ( $T = 20, 30, 40,$  and  $50^\circ\text{C}$ ) as a function of pressure. Points  $a$  and  $b$  delimit low-pressure phase region. Points  $b$  and  $c$  designate phase transition region. Points  $c$  and  $d$  determine high-pressure phase region. Lowest curve corresponds to  $T = 20^\circ\text{C}$ . Highest curve applies to  $T = 50^\circ\text{C}$ .

raised. From measurements carried out by the authors it follows that the density of the olive oil decreases monotonically with increasing temperature. A similar decrease in the density of the olive oil as a function of temperature (at atmospheric pressure) was stated in the works: Coupland and McClements (1997), Guignon et al. (2009), Werner et al. (2008).

The authors also discovered experimentally that, similarly as in the work (Coupland & McClements, 1997), the speed of sound in olive oil decreases monotonically with increasing temperature. Furthermore, our research indicate that the speed of sound in olive oil increases piecewise monotonically with pressure augmentation.

Discontinuities in measured and calculated values of physicochemical parameters as a function of pressure point to the presence of phase transitions in olive oil. These ultrasonic measurements of physicochemical parameters are very important because high-pressure methods are often used during food manufacture, processing and conservation. High mechanical energy introduced to the system leads to changes in the molecular equilibrium in media under pressure. Therefore, the mechanisms, kinetics, and structures of molecular and cellular systems are modified. As a result, many pressure-induced phenomena can occur (Delgado, Kulisiewicz, Rauh, & Benning, 2010). Phase transitions can modify significantly the molecular structure and, consequently, affect the texture and sensory characteristics of food products (LeBail et al., 2003). Therefore measuring the sound velocity in the liquid at high pressure enables to control the quality of food products subjected to high-pressure technological processes, and to understand the nature of physicochemical behavior and intermolecular interactions in edible oils.

Direct measurements of the physicochemical properties of liquid foodstuffs 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 (e.g., with expanded relative uncertainty of the order of  $\pm 0.5\%$ ) over wide ranges of pressure and temperature. Ultrasonic methods were also used to control the degree of purity of edible oils at atmospheric pressure (Aouzale et al., 2010) and their quality (Mulet, Benedito, Golás, & Cárcel, 2002). Described in this paper the method enables the extension of these measurements to high hydrostatic pressure range.

Kinetics of phase transition in olive oil at various temperatures has also been investigated. The results obtained in this study for the olive oil can be compared with the results obtained previously by the authors for olive oil constituents: triglycerides and diglycerides (Kietczyński et al., 2011, 2012). In triacylglycerol at 20 °C, the phase transition occurred in the same pressure range as in the case of examined olive oil. In diacylglycerol phase transition started at about 210 MPa. The transformation time (including induction time) for olive oil was about 6 h, for triacylglycerol was equal to about 40 min, and for diacylglycerol was approximately 20 min. The corresponding transformation times of olive oil and its constituents augment with increasing temperature. For example, at temperature 50 °C, the duration of the phase transition (including induction time) of the olive oil was 25 h. These differences in the kinetics of the phase transition are associated with different molecular structures of the individual constituents (i.e., monoglycerides, diglycerides, triglycerides etc.), and their intermolecular interactions occurring within multi-component oils (such as olive oil), during the course of phase transition.

## 5. Conclusions

The origin of this study was motivated by the lack of thermodynamic parameters of olive oil under high pressure and at different temperatures. Knowledge of these parameters is

indispensable for numerical modeling and optimization of high-pressure food processing and preservation (Aparicio, Otero, Sanz, & Guignon, 2011).

In this paper, the results of measurements of the phase velocity of the longitudinal ultrasonic wave and the density of the olive oil with known composition are presented. Measurements were conducted in a wide range of hydrostatic pressure, up to 600 MPa, for various values of temperature. The key factors that determine the speed of the ultrasonic wave in a liquid are adiabatic compressibility and intermolecular free path length (Priya, Nithya, Velray, & Kanspan, 2010). Using the measured sound speed and density data, the authors calculated adiabatic compressibility, isothermal compressibility, and intermolecular free length, as a function of pressure at various temperatures (isotherms).

Moreover, the kinetics of liquid-to-solid phase transition (crystallization) in olive oil was investigated. The results obtained show a strong influence of pressure and temperature on the kinetics of phase transitions in olive oil. As the temperature increases, higher pressures must be used to initiate phase transition. Moreover, the induction time and the transition time are longer. As the temperature is raised, the intermolecular free path length increases. Since the intermolecular free path length is inversely proportional to the sound speed, therefore with increasing temperature the sound speed decreases.

Under conditions of high pressure, after the phase transition, the molecular structure of the olive oil is changed. High-pressure phase of olive oil is more like a solid medium and forms a solid-like phase. The molecules are more densely packed.

Measurements of sound speed and density in edible oils as a function of pressure and temperature enable to evaluate some useful physicochemical properties and to investigate high-pressure liquid-to-solid phase transition in the oils involved. Changes in the time-of-flight, and consequently in the sound speed, can be observed with much higher resolution than corresponding changes in the oil density. Therefore, observation of changes in the speed of sound seems to be more reliable indication of the occurrence of the phase transition.

The results of this study are a novelty. Presented in the paper, the ultrasonic method can also be used to investigate (at high-pressure conditions) the composition, purity, and quality of other liquid foodstuffs (e.g., fruit juices), not only the fats and oils. The results obtained can be useful for designing and optimizing new methods of food control, processing, and conservation, especially in high-pressure food processing.

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