POSTĘPY AKUSTYKI

AKUSTYKI
Advances
in Acoustics
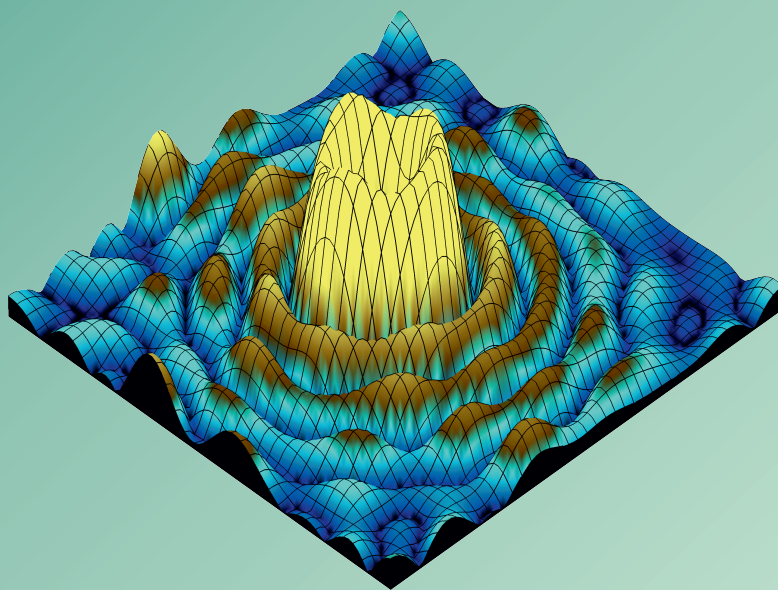
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Mirosław Meissner

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Przedmowa

Akustyka jest nauką żywą i nieustannie rozwijającą się, a dynamiczny postęp techniczny stworzył dla akustyki olbrzymie możliwości badawcze w skali mikro i makro, dzięki czemu możemy uzyskać wiele cennych informacji o strukturze materii, materiałach, konstrukcjach, a także o organizmach żywych, w tym organizmie człowieka. Należy podkreślić interdyscyplinarny charakter akustyki, której rozwój wymaga nie tylko konieczności ujęcia zjawisk od strony fenomenologicznej, lecz także poszukiwania ich interpretacji matematycznej i fizycznej oraz rozpatrywania zjawisk akustycznych z punktu widzenia innych dyscyplin naukowych. Jest to możliwe przez powiązanie akustyki z osiągnięciami dyscyplin naukowych z zakresu nauk ścisłych, technicznych, biologicznych i medycznych, a także nauk humanistycznych.

Niniejsza monografia zawiera 55 recenzowanych rozdziałów wielu autorów, przedstawiających swoje najnowsze badania z zakresu akustyki biomedycznej, akustyki budowlanej, akustyki fizycznej, akustyki mowy, akustyki muzycznej, akustyki środowiska, akustyki wnętrz, badania materiałów, bioakustyki, elektroakustyki, hydroakustyki, przetwarzania sygnałów, psychoakustyki, ultradźwięków i walki z hałasem. Prace te zostały zaprezentowane 13–16 września 2016 roku na LXIII Otwartym Seminarium z Akustyki w Białowieży organizowanym przez Oddział Warszawski Polskiego Towarzystwa Akustycznego.

Redaktor wyd.: Mirosław Meissner

Preface

Acoustics is the active and constantly developing science and dynamic technical progress has created tremendous opportunities for acoustics research at micro and macro scale. Thanks to it we can obtain many valuable information about structure of matter, materials, constructions and also about living beings including human body. The interdisciplinary nature of acoustics must not be forgotten as its development requires not only the approach to the phenomena from the phenomenological point of view but also the search of its mathematical and physical interpretation and the consideration of acoustical phenomena from the perspective of other science disciplines. It is possible by the interrelation of acoustics and the achievements of scientific disciplines in the field of science, technical, biological and medical sciences as well as humanities.

This monograph includes 55 reviewed chapters of many authors presenting the resent research in the field of biomedical acoustics, building acoustics, physical acoustics, speech acoustics, musical acoustics, environmental acoustics, room acoustics, non-destructive testing and evaluation, bioacoustics, electroacoustics, hydroacoustics, signal processing, psychoacoustics, ultrasound and noise control. The above mentioned works were presented at 63rd Open Seminar on Acoustics in Białowieża (13–16.09.2016) organized by the Warsaw Division of the Polish Acoustical Society.

Editor: Mirosław Meissner

Andrzej BALCERZAK*

SIMILARITIES AND DIFFERENCES OF PHYSICOCHEMICAL PROPERTIES OF THE DI- AND TRIACYLGLYCEROLS UNDER HIGH PRESSURE EVALUATED FROM THE RESULTS OF ULTRASONIC MEASUREMENTS

Two samples of triacylglycerols i.e., olive oil and triolein, and one sample of diacylglycerol were investigated. In the course of compression, the density of the samples was determined by measurements of the change of piston position in pressure chamber and volume correction due to chamber expansion under pressure. The speed of sound was calculated from the time of flight of ultrasonic impulse between emitting and receiving transducers placed in the high pressure chamber. The adiabatic compressibility, the intermolecular free length, the molar volume, the van der Waals' constant b and the surface tension were calculated from the density, the speed of sound and the average molecular mass. All tested liquids undergo the high-pressure phase transition. Discontinues of the measured isotherms of the physicochemical parameters of the investigated oils indicate the presence of the high-pressure phase transitions. Moreover the change of pressure during the phase transition was measured. The fundamental difference in the molecular structure of these acylglycerols influences significantly on their behavior under high pressure.

1. INTRODUCTION

Acylglycerols are esters of glycerol and fatty acids. Depending on the number of the esterified hydroxyl groups in glycerol, the molecules of acylglycerols can contain three, two or one fatty acid moieties. This class of chemical compounds has a fundamental importance as foodstuffs and as components for production of surfactants, emulsifiers and biofuels. Their signification for the fuel industry is due to possibility of the conversion to methyl- or ethylesters and their use as the fuel for diesel engines.

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High-pressure physicochemical properties of acylglycerols play important role in food, chemical and fuel technological processing since the extensive application of high pressure processes for their conversion, conservation and preservation [1, 2]. Lack of the data for these parameters is great problem in the design of technological lines and proper leading of production. Physicochemical properties of acylglycerols and their changes caused by high hydrostatic pressure are important to study molecular structures and interactions of acylglycerols. Among others this kind of study becomes significant for acylglycerol metabolism and their nutritional values due to increasing production of high-pressure preserved foodstuffs.

Sound speed is linked with many physicochemical parameters of liquids. Evaluation of physicochemical parameters of liquids under high pressure is extremely difficult. On the other hand the sound speed can be measured at high pressure relatively easy. In this way from high-pressure measurements of the sound speed and the density, the physicochemical parameters of liquids under high pressure can be relatively easy evaluated.

The aim of this work is to measure the density and the sound speed under high-pressure, and subsequently to evaluate physicochemical parameters such as: adiabatic compressibility, intermolecular free length, molar volume, van der Waals' constant b and surface tension and compare their behavior for triacylglycerols (TAG) and diacylglycerol (DAG). These kinds of study play important role because of the lack of the values of the physicochemical parameters for liquids under high pressure. As mentioned above, knowledge of the behavior of the physicochemical parameters during high pressure compression and possible occurrence of the phase transition is very valuable from scientific (molecular structures and their changes in the course of pressure increasing) and technological (designing of chemical, fuel and food installations and their proper operation) points of view.

By using ultrasonic methods we revealed the occurrence of high-pressure phase transition in the investigated liquids. Discontinuities in the measured isotherms of density and sound speed versus pressure in all investigated liquids indicate the presence of liquid to solid-like transformations.

Measurement of the sound speed and density of the investigated liquids were performed in the pressure range from atmospheric pressure to 600 MPa and at temperature 20°C.

2. MATERIALS

2.1. TAG SAMPLES

TAGs are esters of the trihydric alcohol glycerol in which all three hydroxyl groups are esterified with fatty acids. Two kinds of TAG were used for measurements:

a) Triolein (Sigma-Aldrich, practical grade >65%)
b) Olive oil

This olive oil was produced in Spain with a high content of triacylglycerols of oleic acid (76,8%) – Table 1. The composition of the tested oil is analyzed by means of gas chromatography method using Hewlett-Packard HP 6890 device with Flame Ionization Detector and high-polar column BPX70. This analysis was made following the AOCS Cd 11b-91 method and was performed according to the ISO 5508 and ISO 5509 norms. The results of this analysis are shown in table 1 [3].

Table 1. Chemical composition of investigated olive oil

fatty acid	C14:0	C16:0	C16:1	C17:0	C17:1	C18:0	C18:1c	C18:2ct/tc
% in olive oil	< 0.1	11.02	1.01	0.1	0.1	3.4	76.8	< 0.1
fatty acid	C18:2cc	C18:3ccc	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

In investigated olive oil, the dominant component is oleic acid (C18:1 *cis*). The second, third, fourth and fifth main components are palmitic (C16:0) and linoleic (C18:2 *cis-cis*), stearic (C18:0) and palmitoleic (C16:1) acids, respectively. Other fatty acids are presented in small amount (< 1%).

2.2. DAG SAMPLE

DAGs are esters of the trihydric alcohol glycerol in which two of the hydroxyl groups are esterified with fatty acids.

DAG oil used for testing is composed of 82% of diacylglycerols and 18% of triacylglycerols, with negligible content of monoacylglycerols. The analysis conducted analogically as for TAG sample, gave results presented in Table 2 [4].

Table 2. Chemical composition of tested DAG oil

fatty acid	C14:0	C16:0	C16:1	C17:0	C17:1	C18:0	C18:1c	C18:2cc
% in DAG	0.1	4.5	0.5	0.1	0.1	2.5	59.1	19.6
fatty acid	C18:3ccc	C20:0	C20:1	C20:0	C22:1	C24:0	C24:1	
% in DAG	8.9	1.9	1.0	0.1	1.2	0.3	0.1	

The prevailing component is oleic acid (C18:1 *cis*). The second, third, fourth, fifth and sixth main components are linoleic (C18:2 *cis-cis*), linolenic (C18:3 *cis-cis-cis*), palmitic (C16:0), stearic (C18:0) and arachidic (C20:0) acids, respectively. Other fatty acids are presented in small amount (≤ 1,2%)

3. METHODS

Detailed description of the high-pressure measuring setup is presented in [5-7]. Pressure in testing chamber is produced by a manually driven hydraulic press. Pressure and temperature sensors are placed inside the pressure chamber within the investigated oil sample. The volume of chamber equals 22 cm^3. The change of electrical resistance of calibrated manganin sensor is used to measure the pressure inside chamber. Volume changes of the sample under pressure were calculated from the piston displacement registered by a digital caliper. Corrections related to the chamber expansion were evaluated from the Lame equations. These two facts allowed calculating the density of the sample under pressure since the mass of the sample was not changed during the measurements. The sample density under atmospheric pressure was determined by means of U-shape tube densitometer (MG-2, Unilab, Poland). Temperature was kept constant by a circulation of thermostatic liquid in jacket of the chamber supplied by a precision thermostat (Julabo Labortechnik, Seelbacg, Germany).

The pressure inside the chamber was measured by a 100 Ω manganin wire sensor [8]. The resistance of the manganin wire sensor was measured using an NI 4065 multimeter computer card (National Instruments Corp., Austin, TX, USA). The pressure was increased in 10 MPa steps and with a time interval sufficient to establish the thermodynamic equilibrium of the liquid sample.

Before measurements, the setup was calibrated by using distilled water as tested liquid. Subsequently and exact values of the distance between transducers is calculated using known values of speed of sound in water as a function of pressure.

Speed of sound was determined from the time of flight of ultrasonic waves between two transducers. The sending and receiving transducers were made from two 5 MHz LiNbO3 plates (Y36 cut, Boston Piezo-Optic Inc., Bellingham, MA, USA). The sending transducer is driven by a signal from the TB-1000 pulser-receiver computer card (Matec Instrument Companies Inc., Northborough, MA, USA). The electric signal was changed in the ultrasonic one by the sending transducer. Then the ultrasonic signal passed through the sample of the investigated liquid and was changed in electrical signal by the receiving transducer. This signal was processed by the PDA-1000 digitizer computer card (Signatec, USA). To increase the signal-to-noise ratio, each single measurement was repeated 1024 times and averaged. The cross-correlation method [9] was applied to evaluate the time of flight of the signal. The experimental setup was calibrated by measurements carried out in distilled water.

The speed of sound, c, is calculated from Eq. 1:

$$c = \frac{l}{t} \tag{1}$$

where l is distance between transducers and t is time of flight of the ultrasonic signal.

The density of the measured liquids under pressure, ρ, was evaluated from the formula (2):

$$\rho = \frac{m}{V - \Delta V} \tag{2}$$

where: m is the mass of the sample, V is the initial volume of the sample and ΔV is the change of the sample volume resulting from the piston displacement caused by the applied pressure.

4. RESULTS AND DISCUSSION

4.1. DENSITY

The results of direct measurements of density, ρ, as a function of pressure, are presented in Fig.1.
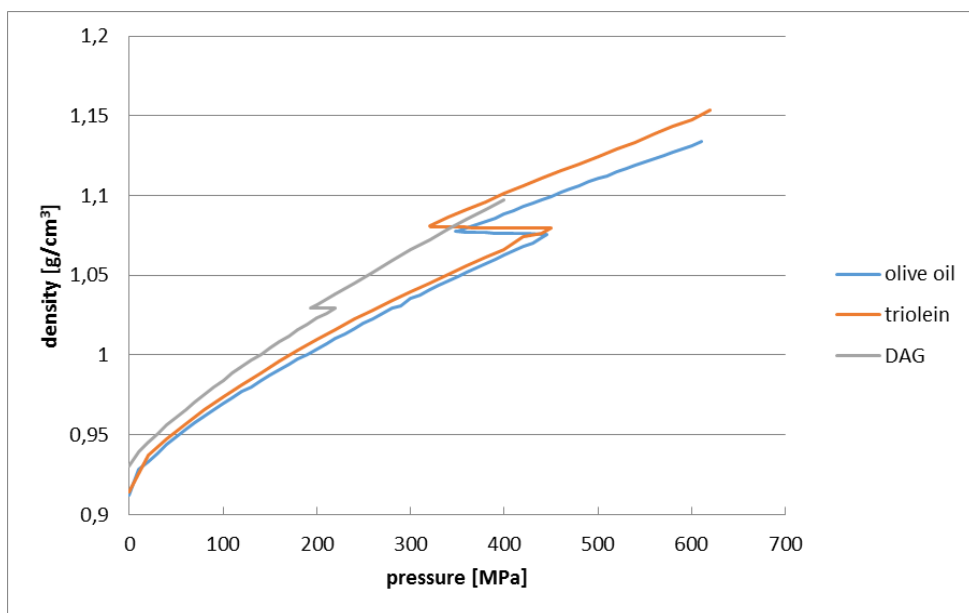

Fig.1. Plots of densities as a function of pressure.

The behavior of density versus pressure is similar for all investigated liquids except the fact that the phase transformation (flat part of the curve) occurs at lower pressure for DAG oil. That fact is a consequence of the molecular structure, which is more compacted for olive oil and triolein than for DAG oil. Density is almost constant dur-

ing the phase transformation, which manifest itself in that the distance value indicated by the caliper does not change. Thus this transformation is isochoric one in the experimental conditions.

4.2. SPEED OF SOUND

The results of the measurements of speed of sound, c, as a function of pressure, are presented in Fig. 2.
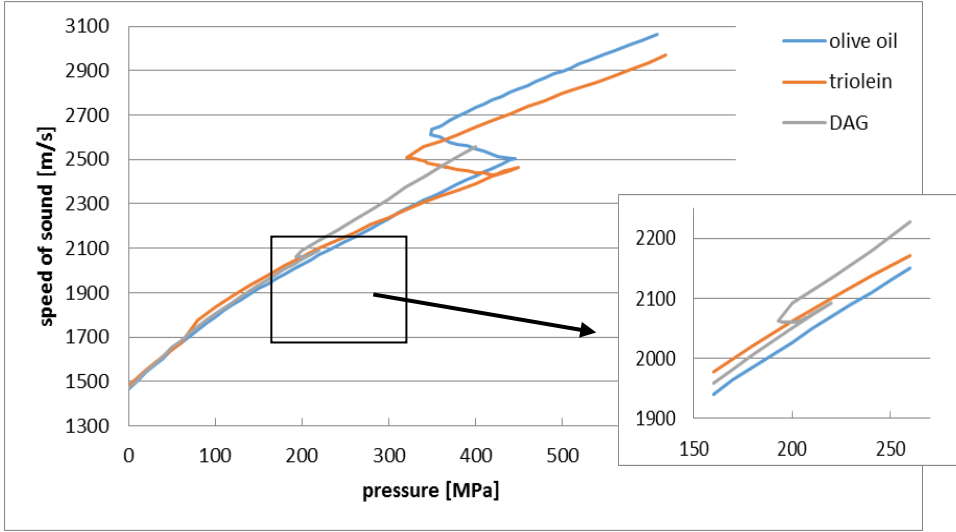

Fig. 2. Plots of speed of sound as a function of pressure for investigated liquids.

In the case of speed of sound, all tested liquids exhibit the quantitative similarity up to phase transformation while they are compressed. In phase transformation the speed of sound for triolein initially decreases following low-pressure phase compression curve (from 450 MPa to 420 MPa). Subsequently the speed of sound increases and the pressure decreases spontaneously. The speed of sound for the olive oil increases in the whole pressure range in the phase transition region. The behavior of DAG is the same like that for triolein. However, the change in sound speed in DAG sample is remarkably smaller than that in triolein sample.

4.3. ADIABATIC COMPRESSIBILITY

The adiabatic compressibility, β_S, is calculated as:

$$\beta_S = \frac{1}{c^2 \rho} \tag{3}$$
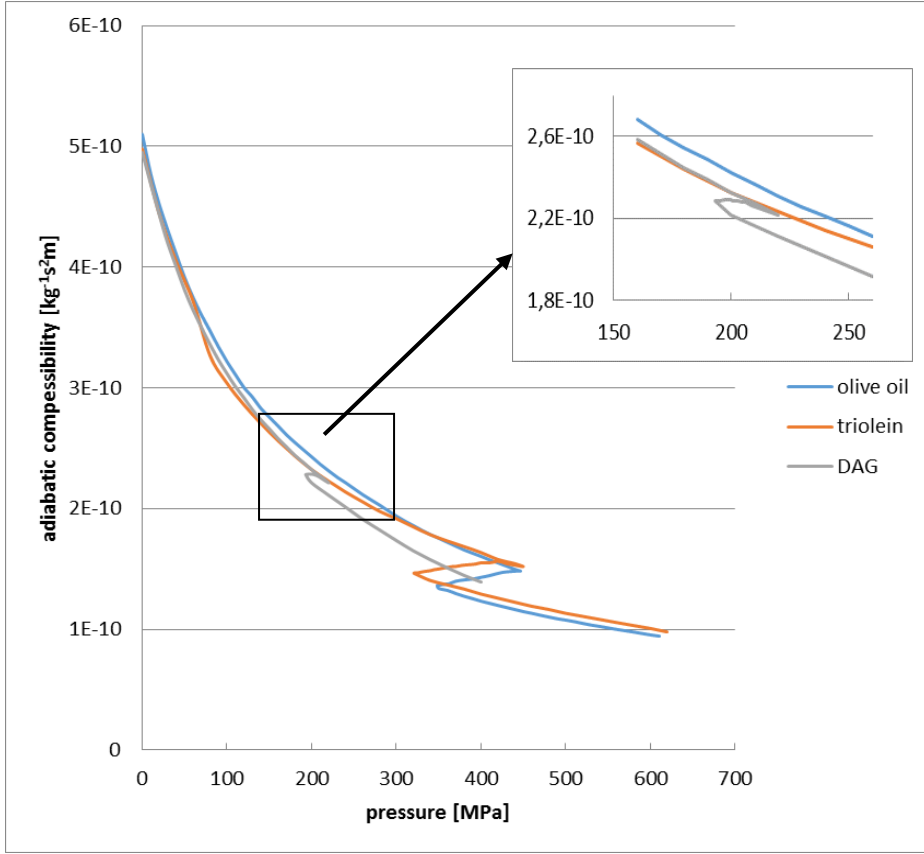
The obtained results are presented in Fig. 3.

Fig. 3. Adiabatic compressibility as a function of pressure.

From comparison of Figs. 3 and 2 one can conclude that the density does not influence significantly the behavior of adiabatic compressibility when pressure increases.

4.4. INTERMOLECULAR FREE LENGTH

The intermolecular free length, L_f, is calculated from the formula:

$$L_f = \frac{K}{c\rho^{1/2}} = K\sqrt{\beta} \tag{4}$$

Where: K is Jacobson constant determined by the dependence $K = (93.875 + 0.375 \cdot T) \cdot 10^{-8} \, [(m \cdot kg)^{1/2}/s]$. T denotes absolute temperature in Kelvin.

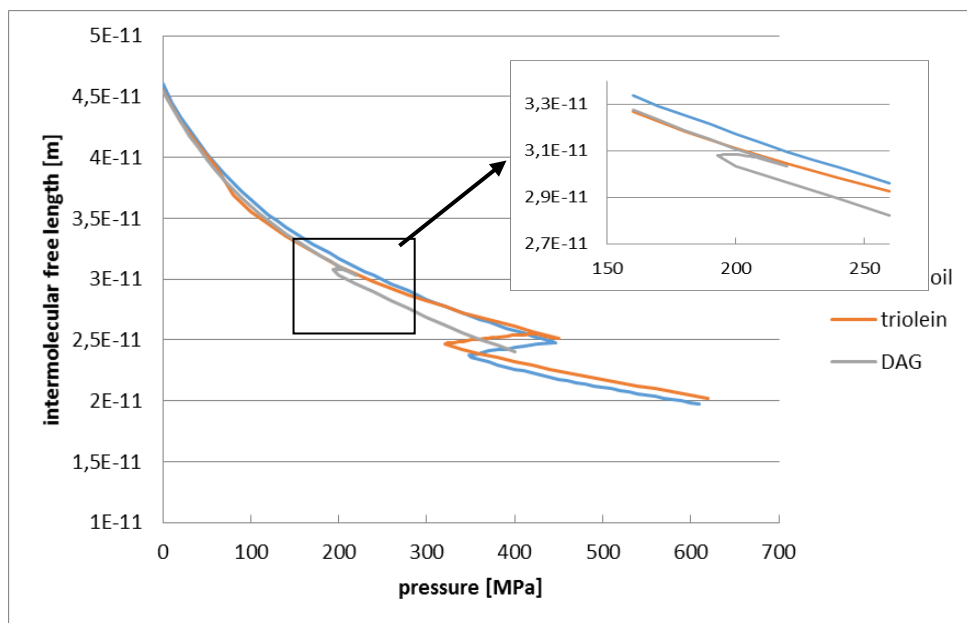The dependence of L_f on pressure is shown in Fig. 4.

Fig. 4. Intermolecular free length vs pressure.

The intermolecular free length, L_f, decreases monotonously when the pressure increases, except the region of phase transformation. For the low range of pressure before the phase transformation the courses of L_f almost overlap for all investigated liquids. Distances between molecules become shorter and the liquid structure adjust to the external condition – increasing pressure. In the region of the phase transformation, L_f and pressure decrease for the olive oil and triolein. The drop of L_f is small. This means that the small changes of L_f at constant volume involved by rearrangement of the molecular structure towards more compact one cause significant decrease of pressure. In the case of DAG oil the different behavior can be noticed in the phase transformation region. The intermolecular free length slightly increases and pressure decreases in this region. These different behaviors of both TAGs compare to DAG and the greater pressure change during phase transition for TAGs than DAG are caused by smaller steric hindrances in DAG structure than in TAG one. It is quite understandable taking into account that the molecules of TAG contain one more moiety of the long chain fatty acid than DAG ones.

The molar volume, V_M, was calculated according to the formula:

$$V_M = \frac{M}{\rho}$$

(5)

where: M is molar mass (see Fig. 5).

Mean molar masses of investigated liquids i.e., olive oil, triolein and DAG oil were calculated from the mass ratios and molecular masses of the components and equal 0.8756, 0.8855 and 0.6550 kg mol^{-1}, respectively.
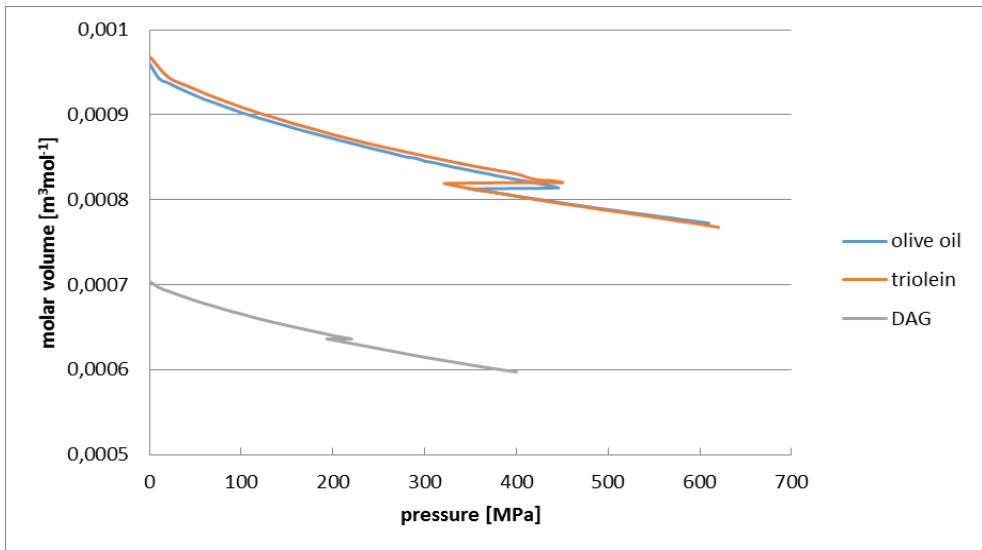

Fig. 5. Molar volume vs pressure.

4.6. VAN DER WAALS' CONSTANT

The van der Waals' constant, b, which takes into account the molecule dimensions, is the volume of one mol of molecules only, is determined from:

$$b = \frac{M}{\rho}\left\{1-\left(\frac{RT}{Mc^2}\right)\left[\left(1+\frac{Mc^2}{3RT}\right)^{1/2}-1\right]\right\}$$

(6)

where $R= 8.314$ JK^{-1}mol^{-1} is the universal gas constant. The changes of values of parameter b on pressure are presented in Fig. 6.
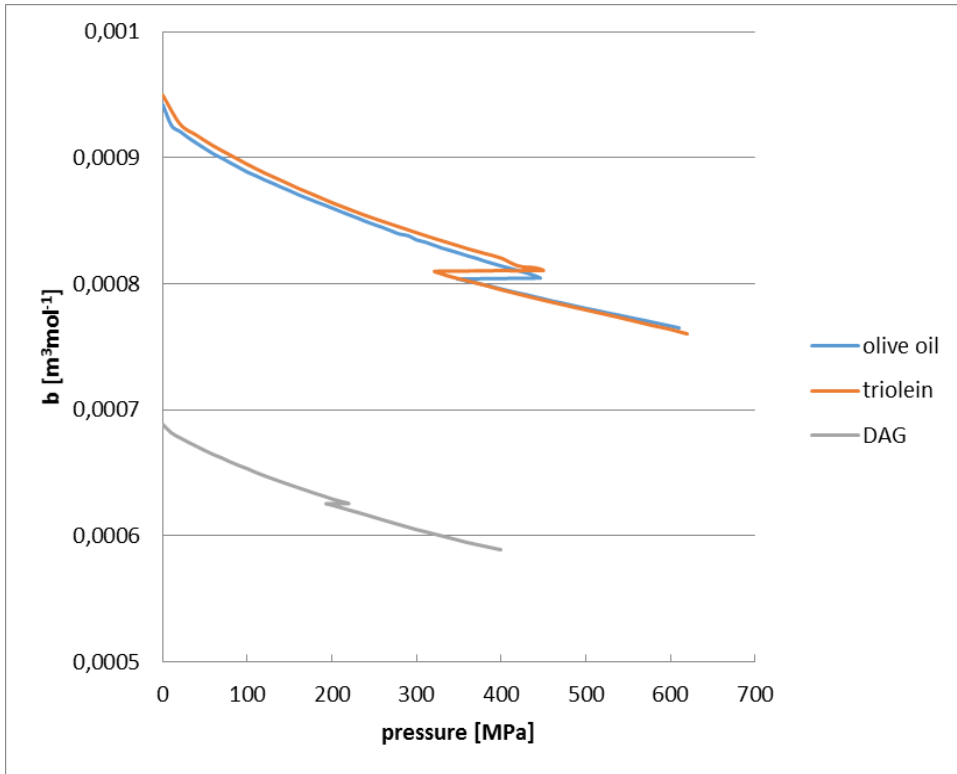

Fig. 6. Dependence of van der Waal's constant b on pressure.

For triacylglycerols i.e. olive oil and triolein, values of the parameter b and their high-pressure behavior are similar. This fact is understandable since the similarity of molecules of main components of these liquids. The molecules of DAG are smaller because they contain two moieties of fatty acids. Therefore, for the DAG oil the values of the parameter b are lower than that for olive oil and triolein.

It is valuable to compare the product of subtraction of molar volume V_M and van der Waals' constant b for the investigated liquids:

$$V_A = V_M - b \qquad (7)$$

Values of V_A are presented in Fig. 7. According to formula (6) V_A can be considered as volume without molecules for one mole of a substance. Analyzing the plots in Fig. 7 one can notice that for olive oil and triolein the course of V_A against pressure is

similar in the regions before and after phase transition. During phase transition the volume without molecules, V_A, decrease and values of V_A are lower for olive oil than for triolein. This can be related with the composition of both oils. For DAG the values of V_A are distinctly lower than for triacylglycerols. In the region of phase transition the volume without the volume of molecules themselves, V_A, for DAG oil slightly increases, because the molecules of DAG oil components according to their simpler structures are more tractable on pressure constraint than olive oil and triolein.
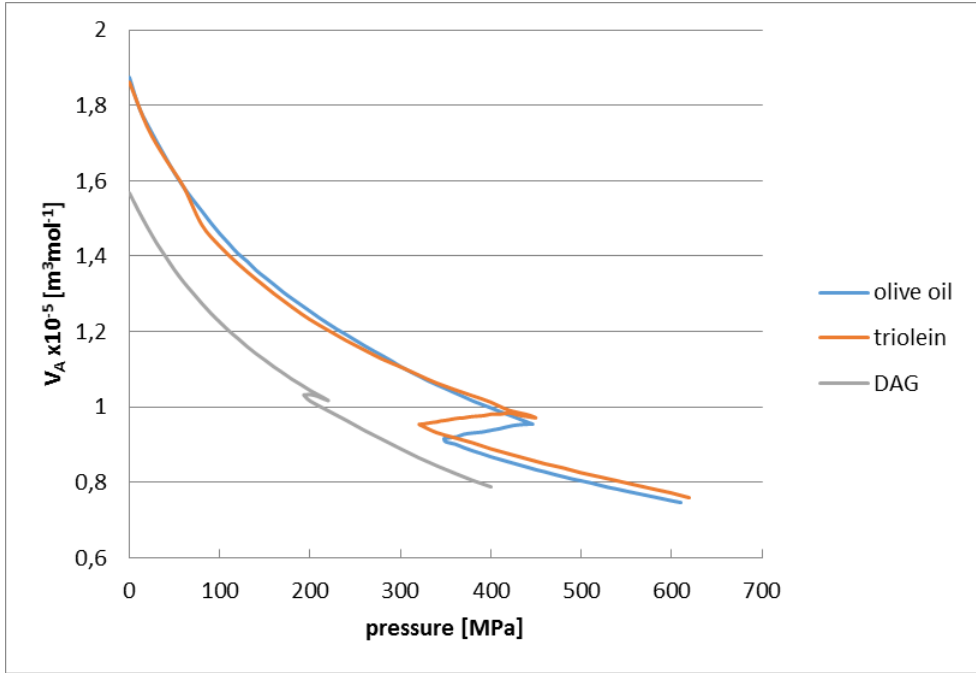

Fig. 7. Parameter V_A vs pressure.

4.7. SURFACE TENSION

Surface tension was calculated from the Auerbach formula [10]:

$$\sigma = 6{,}33 \cdot 10^{-10} \rho c^{3/2} \tag{8}$$

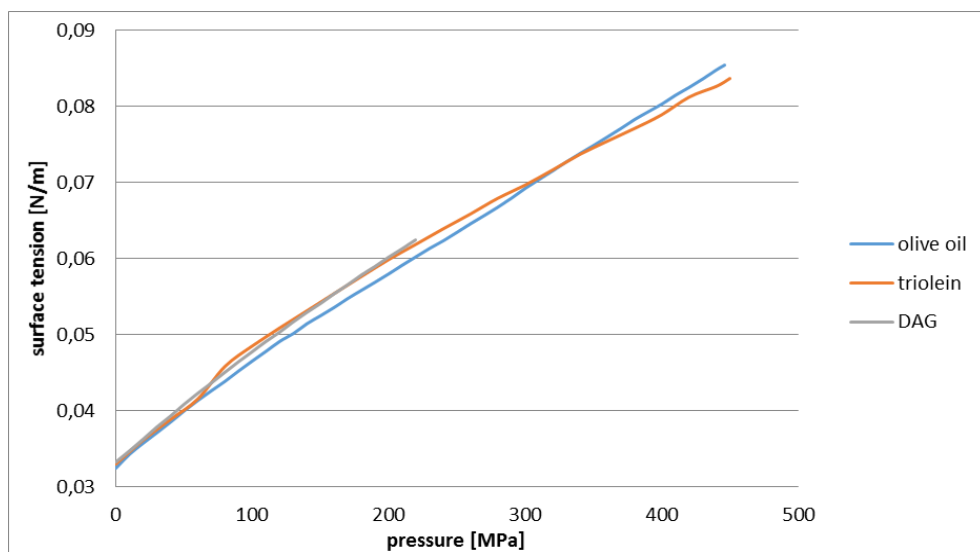The obtained results for the investigated liquids are shown in Fig.8.

Fig. 8. Surface tension vs pressure.

Despite the difference in molecular structure of the investigated liquids the values of the surface tension, σ, with increasing pressure, are similar for both TAGs and DAG oil.

4.8. DEPENDENCE OF PRESSURE ON TIME DURING HIGH-PRESSURE PHASE TRANSITIONS

In Fig. 9 the dependences of pressure on time during phase transition for all investigated liquids are shown.

The big differences of behavior of tested liquids in this region can be easily noticed. For triolein the decrease of pressure is significantly sharper than for olive oil. In olive oil the time before and after the curve inflection is longer than that for triolein. Thus the molecules of the components of olive oil need more time to start the phase transition and achieve the equilibrium state than triolein molecules. For DAG oil the phase transition runs fast and with low change of pressure. The molecular rearrangement of structure containing two fatty acid moieties (DAG) needs shorter time than these with three fatty acid moieties (olive oil and triolein) due to greater complication of molecular structure and steric obstacles.
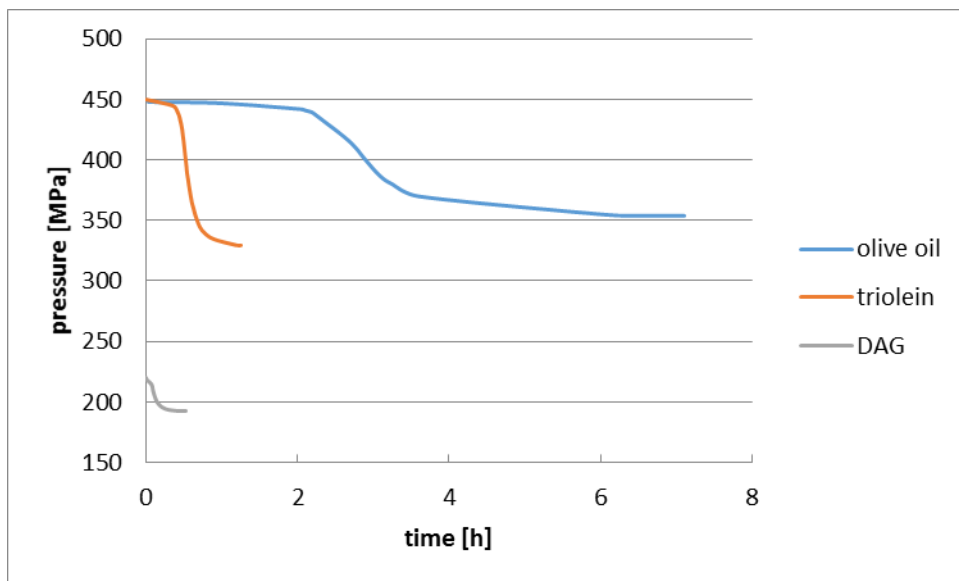
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Fig. 9. Dependences of pressure on time in the course of phase transition.

5. CONCLUSIONS

The origin of this study was motivated by the lack of sufficient information on physicochemical parameters of liquids and changes of their molecular structures under high-pressure conditions.

Knowledge of these parameters is indispensable for numerical modeling and optimization of high-pressure food processing and preservation.

From the ultrasonic measurements in a wide range of hydrostatic pressure the main parameters, i.e. density and speed of sound for considered samples of olive oil, triolein and DAG oil, were obtained experimentally. The following physicochemical parameters of investigated oils were evaluated: adiabatic compressibility, intermolecular free length, van der Waals' constant b and product of subtraction of molar volume V_M and van der Waals' constant b. The analysis of the results shows great differences of the high-pressure behavior of the physicochemical parameters for TAGs and DAG due to their different molecular structure i.e. larger, more stiff and bigger steric hindrances for TAGs than for DAG oil. Small differences of physicochemical parameters between two investigated TAGs i.e. olive oil and triolein, were observed. This phenomenon can be caused by different content of olive oil and triolein main component i.e. oleic acid (C18:1 *cis*) 76,8% and >65%, respectively.

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