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Ultrasonic evaluation of thermodynamic parameters of liquids under high pressure

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***Abstract*—In many technological processes (e.g. in chemical, petrochemical, food and plastics industry) liquids are subjected to high pressures and temperatures. Therefore knowledge of their thermodynamic properties is essential for understanding, design and control of the process technology. Direct evaluation of thermodynamic parameters of liquids under high pressure, using conventional methods, is very difficult. Therefore, these methods are useless in industrial conditions, particularly in on-line control of the technological parameters of liquids. Ultrasonic methods (e.g., sound speed measurements) due to their simplicity and accuracy are very suitable for this purpose. The sound velocity is closely related with numerous thermodynamic properties of liquids. In this paper we report ultrasonic velocity and density measurements (performed by the authors) in diacylglycerol (DAG) oil over a range of pressures and temperatures. On the basis of experimental results (the sound velocity and liquid density versus pressure and temperature) the thermal expansion coefficient, specific heat capacity at constant pressure, isothermal and adiabatic compressibility of DAG oil were calculated as a function of pressure and temperature.**

Keywords*—*sound velocity; thermodynamic parameters of liquids; high pressure; heat capacity; thermal expansion coefficient

I. Introduction

In many technological processes (e.g. in the chemical, food [1], petrochemical [2,3], and plastics [4] industry) processed liquids are subjected to high pressures and temperatures. Therefore, knowledge of their thermodynamic properties is essential for the understanding, design and control of the technological processes. Knowledge of high-pressure thermodynamic properties of fuels and biofuels [5,6] is also indispensable due to the increasing operating pressures in modern fuel injection systems. Direct evaluation of thermodynamic parameters of liquids under high pressure, using conventional methods, is very difficult. Therefore, these methods are useless in industrial conditions, particularly in on-line control of the technological parameters of liquids. 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 sound velocity is closely related with numerous thermodynamic properties of liquids. In this paper ultrasonic velocity and density measurements (performed by the authors) in diacylglycerol (DAG) oil over a range of pressures and temperatures have been performed. DAG oil is very ubiquitous fat in foodstuffs.

The time-of-flight of ultrasonic wave pulses in DAG oil was measured using cross-correlation method. Density values of DAG oil under high pressure were evaluated from the measurement of changes in the volume of pressurized DAG oil sample. On the basis of experimental results (the sound velocity and liquid density versus pressure and temperature) the thermal expansion coefficient, specific heat capacity at constant pressure, isothermal and adiabatic compressibility were calculated as a function of pressure and temperature.

II. Materials and Methods

In this paper we present measurements of the time of flight of the longitudinal ultrasonic wave between the transmitting transducer and receiving transducer by means of the cross-correlation method. 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. The measuring set-up and methods have been described in authors' previous works [7-10]. The expanded relative uncertainty for the sound speed in liquid was equal $\pm$ 0.3% at a 95% confidence level. The expanded relative uncertainty of the density was $\pm$0.05%.

Using the measured values of density and sound velocity, we determined the isothermal and adiabatic compressibility, the thermal expansion

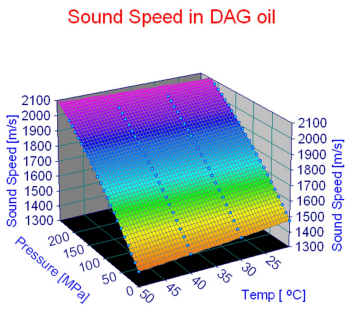

Fig.1. Plots of sound speed in DAG oil as a function of pressure along various isotherms ($T = 20, 30, 40, and\ 50\ °C$), $f = 5\ MHz$.

coefficient, and the specific heat capacity at constant pressure. as a function of pressure for various values of temperatures employing analytical expressions specified in Section III.

DAG oil sample was diacylglycerol oil that was composed of 82% of DAGs and 18% of TAGs (triacylglycerols) with a vestigial amount of monoacylglycerols and free fatty acids. The fractions were determined by means of the gas chromatography method. The analysis was performed according to ISO 5508 and ISO 5509 norms [11].

III. Experimental Results

A. Sound velocity

Figure 1 shows the results of longitudinal ultrasonic wave velocity measurements (frequency 5 MHz) at temperatures: 20, 30, 40, 50 °C. Pressure was applied in increments of 10 MPa up to 220 MPa. Each increase in pressure was followed by an interval of time (5 min), which allowed the DAG oil to achieve the thermodynamic equilibrium conditions.

B. Density

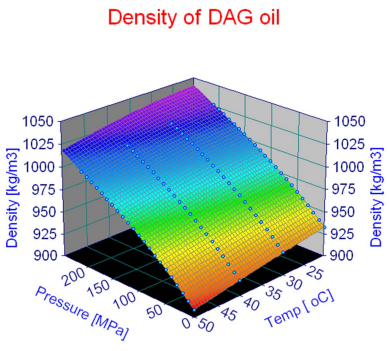

Fig.2. Density of DAG oil as a function of pressure and temperature.

Figure 2 shows the dependence of the density of DAG oil versus pressure and temperature in the case of low-pressure phase.

C. Numerical approximation of the density and sound velocity

Empirical relationships $v(p,T)$ and $\rho(p,T)$ have been approximated by the appropriate functions of two variables (p,T), i.e., the pressure p and the temperature T. Computer software package Table Curve 3D (Systat, USA) was used to perform the curve fittings. Sound velocity and density were approximated by using third order polynomials of two independent variables (p,T):

$$v(p,T) = a + bp + cT + dp^2 + eT^2 + fpT + gp^3 + hT^3 + ipT^2 + jpT^2 \quad (1)$$

where: a = 1556.1007, b = 3.5558133, c = -5.2591231, d = -0.0046743392, e = 0.070266476, f = 0.0082758464, g = 3.8777839e-6, h = -0.0005704745, i = -3.0256387e-5, j = -9.7492135e-6.

Similar approximation was also performed for the density $\rho(p,T)$ of DAG oil.

D. Thermal expansion coefficient

The thermal expansion coefficient α_p was evaluated according to the following formula:

$$\alpha_p(p,T) = \frac{-1}{\rho(p,T)}\left(\frac{\partial \rho}{\partial T}\right)_p \quad (2)$$

The dependence of the thermal expansion coefficient α_p on pressure and temperature is presented in Fig. 3.

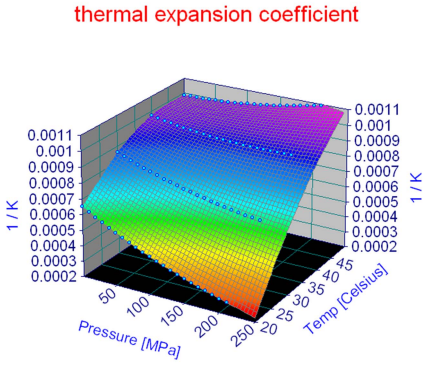

Fig.3. The dependence of the thermal expansion coefficient α_p on pressure and temperature.

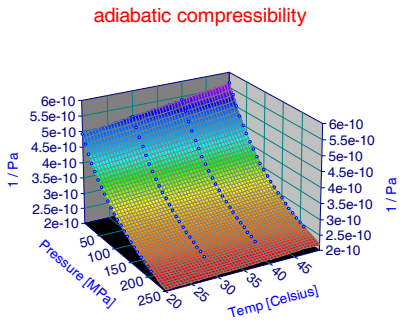

Fig.4. The dependence of the adiabatic compressibility k_s on pressure and temperature.

E. Adiabatic compressibility

Adiabatic compressibility was determined from the expression:

$$k_s(p,T) = \frac{1}{\rho(p,T)\, v^2(p,T)} \tag{3}$$

where: ρ is the density of DAG oil, c is the sound velocity in DAG oil.

The dependence of the adiabatic compressibility k_S on pressure and temperature is presented in Fig.4.

F. Isothermal compressibility

Isothermal compressibility k_T is defined as follows:

$$k_T(p,T) = \frac{1}{\rho(p,T)}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{4}$$

where ρ is the density of DAG oil at a pressure p. T is the temperature in Kelvin.

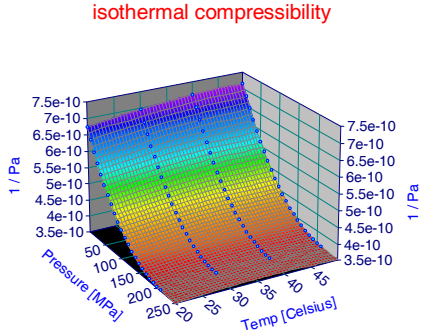

Fig.5. The dependence of the isothermal compressibility k_T on pressure and temperature .

Figure 5 shows the isothermal compressibility of DAG oil as a function of pressure for various values of temperature.

G. Specific heat capacity at constant pressure

Specific heat capacity at constant pressure c_p has been calculated using the following equation:

$$c_p(p,T) = \frac{T\,\alpha_p^2(p,T)}{\rho(p,T)\,(k_T - k_s)} \tag{5}$$

where: T is the temperature in Kelvin, k_T is the isothermal compressibility, k_s is the adiabatic compressibility.

The dependence of the specific heat capacity at constant pressure c_p on pressure and temperature is presented in Fig.6.

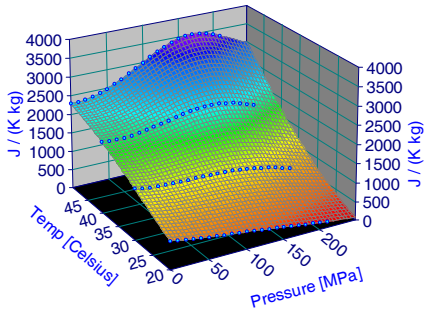

Fig.6. The dependence of the specific heat capacity at constant pressure c_p on pressure and temperature.

IV. Conclusions

The fundamental goal of this work was to evaluate the influence of temperature and high pressure on thermodynamic properties of liquids. The method used for this purpose is based on ultrasonic velocity measurements under high pressures and at various values of temperature. Measurements of sound velocity and density in DAG oil as a function of pressure and temperature enable to evaluate its several useful thermodynamic parameters such as thermal expansion coefficient, specific heat capacity at constant pressure, isothermal and adiabatic compressibility, whose direct measurement, in particular under high pressure is very difficult.

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.

To the authors' best knowledge the results presented in this paper are a novelty and have not been reported in the scientific literature. Hitherto, similar measurements of physicochemical properties of liquids have not been performed in such a wide range of pressures.

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