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INFLUENCE OF TEMPERATURE ON THE PHYSICAL PROPERTIES OF VEGETABLE OILS

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Abstract. *The aim of this study is to investigate the influence of temperature (20 - 80°C) on the physical properties of vegetable oils and to establish some correlations between them. In this study were studied eight types of vegetable oils as: olive oil, corn oil, sunflower oil, grape seeds oil, squash oil, hazelnut oil, peanut oil and sesame oil. The temperature influences negatively almost all the physical parameters measured (exception isentropic compressibility and Rao´s molar sound function). A master curve of the correlation between the experimental data of oil samples density, surface tension and ultrasound velocity was achieved (R^2 = 0.996). The correlation between surface tension and viscosity was made using Pelofsky, modified Pelofsky, exponential and polynomial models, the second one fits better the experimental data.*

Keywords: *density, oils, surface tension, temperature, ultrasonic parameters, viscosity*

1. Introduction

The physical properties of fluid are different in nature but whose values need to be known for a wide variety of industrial and physicochemical processes. Surface tension affects important stages in such production processes as catalysis, adsorption, distillation and extraction. Viscosity is important in processes involving a flow of fluids extensively [1]. Ultrasonic velocity is usually correlated with density fluctuations of pure liquid; thereby it is closely related to compressibility, which is a response function of the density to the mechanical pressure [2].
One of the models used for the correlation of surface tension was proposed by Pelofsky [3]. The Pelofsky model can be applied for the organic and inorganic phases of pure and mixed components. The model involves two adjustable coefficients, whose values may depend in the temperature range being considered [1]. The influence of the temperature on ultrasonic velocity was studied [4], however the correlation between different physical properties of vegetable oils have not been reported to the authors knowledge.
The aim of this study is to study the influence of temperature on the physical properties of vegetable oils (density, viscosity, ultrasonic parameters and surface tension) and to establish some correlations equations between them.

2. Experimental

Materials

For this study were analyzed eight different types of vegetable oils as: olive oil, corn oil, sunflower oil, grape seeds oil, squash oil, hazelnut oil, peanut oil and sesame oil. They were purchased from the local market of Romania.

Density measurements
Density (ρ) of the oils samples was measured using pycnometer with an accuracy 10^{-4} gm/cc. The calibration of pycnometer was made with ultrapure water. Temperature was kept constant within ±0.1 °C using PID controller and circulating water using thermo static-fluid bath. The density of the eight samples of oils was measured at 20, 30, 40, 50, 60, 70 and 80 °C. The values of parameters were expressed as the mean ± standard deviation to a confidence interval for mean of 95 %.

Ultrasonic velocity measurement
The ultrasonic speed measurement was carried out using a flow detector USM 35 X (GE Measurement and Control, USA) with a dual-element (TR) probe working at 4 MHz. The measurements were carried out at 20, 30, 40, 50, 60, 70 and 80 °C. The values of parameters were expressed as the mean ± standard deviation to a confidence interval for mean of 95 %.

Viscosity measurement
Viscosity measurements were carried out on the oil samples at different temperatures (20, 30, 40, 50, 60, 70 and 80 °C), with Hoppler viscometer using glass ball, with temperature controlled water bath. The oil sample was allowed to reach the desired temperature 20 min. Each measurement was taken in duplicate. The values of parameters were expressed as the mean ± standard deviation to a confidence interval for mean of 95 %.

Surface tension determination
The surface tension was computed using the Auerbach´s equation [5]:

$$u = \left(\frac{\sigma \times 10^{10}}{6.33 \times \rho}\right)^{2/3} \quad (1)$$

where u is the ultrasonic velocity (m/s), σ is the surface tension in N/m and ρ is the density in kg/m^3. Therefore, for the calculation of the surface tension, first we measured the ultrasonic velocity and density and later on by using the Auerbach equation we were able to compute the surface tension.

Prediction accuracy
The mean relative deviation modulus, *D*, was used to verify the suitability of model for experimental data:

$$D\% = \frac{100}{n}\sum_{i=1}^{n}\frac{|x_{exp,i} - x_{cal,i}|}{x_{exp,i}} \quad (2)$$

where n is the total number of data in the number of data in the sample. Subscript exp. and cal. denote experimental and calculated values, respectively. X represents density, ρ, or viscosity, η, surface tension, σ, and ultrasonic velocity, u.

Statistical analysis
The parameters were fitted to the proposed equation using SPSS trial version and Excel 2007.

3. Results and discusion

Effect of temperature on density
The measured densities of oils samples from 20 – 80 °C in function of temperature are presented in figure 1. The density of oils samples was smaller than water density in all the samples; it ranged (20 - 80 °C) between 866.9533 – 925.1260 kg/m^3. The density is slightly influenced by temperature; the values of the oils density decreased with the increasing of temperature.
The evolution of density with temperature shows a small change of the density with the change of the temperature of the solution. The evolution of the density with temperature was subjected to linear regression to see its prediction using the eq. 3:

$$\rho = a + b \cdot T \qquad (3)$$

where ρ – density (kg/m^3), a and b are constants, and T – temperature (°C).

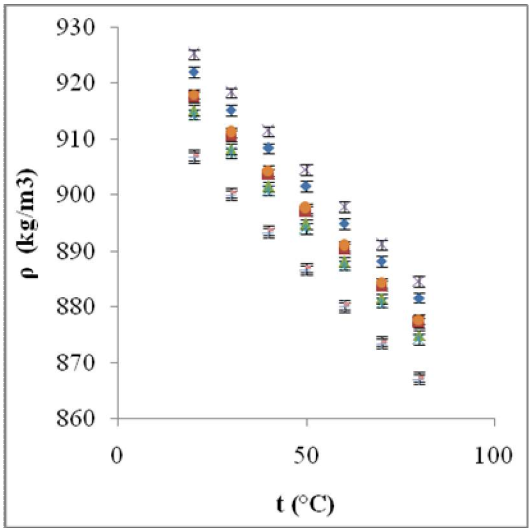

Fig. 1. Density of vegetable oils in function of temperature: ◆ corn oil, ▪ sunflower oil, ▲ squash oil, × grape seed oil, ✱ sesame oil, ● olive oil, + ground nut oil, ‒ peanut oil

The prediction of the equation 3 is in good agreement with the experimental values. All the oils' densities were good predicted using this equation, all the regression coefficients ranged between 0.991-0.999. The values of a ranged between 919.8 and 938.5, while b ranged between -0.662 and -0.676 respectively.

Effect of temperature on viscosity

The viscosity measurements were made at 20 – 80 °C. In order to obtain the fitting results, the viscosity data were plotted into two different ways: viscosity, η, versus temperature, T. The plot is presented in figure 2. Viscosity is a temperature function, it decreases with the increasing of temperature.

Correlations were made to allow the prediction of viscosity of the oils samples. The correlations of viscosity were as a function of temperature using polynomial fitting by means of the experimental data. The following expression was used for the regression equations of the experimental data:

$$\eta = c + d \cdot T + e \cdot T^2 \qquad (4)$$

where η is the viscosity in Pa·s, T is the temperature in °C, and e, f, g are fitting parameters.

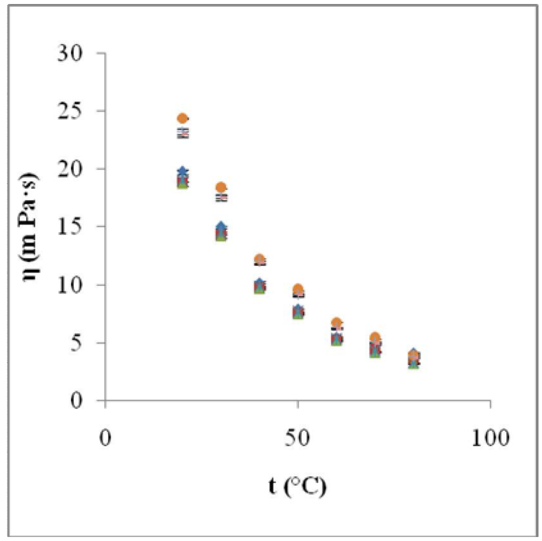

Fig. 2. Viscosity of vegetable oils in function of temperature: ◆ corn oil, ▪ sunflower oil, ▲ squash oil, × grape seed oil, ✱ sesame oil, ● olive oil, + ground nut oil, ‒ peanut oil

The regression coefficients ranged between 0.959 and 0.987. The parameters values of equation 5 ranged between: e 29.803 and 116.646, f -5.391 and -1.317 and g 0.015 and 0.062, respectively. The parameters values of equation 6 ranged between: h 315.9 and 19778, i -500.7 and -8.131 and j 0.052-3.170, respectively. The mean relative deviation modulus between the prediction and experimental values and average ranged between 1.161 and 5.514%.

Effect of temperature on ultrasonic parameters

The ultrasonic velocity ranged between 1301-1489 m/s. In order to obtain the ultrasonic velocity data of oils samples at any temperatures, the experimental data were expressed in a form of ultrasonic velocity, u,

versus temperature, T. These results are presented in figure 3.
It can be observed that the ultrasonic velocity is linear with regard to temperature. The ultrasonic velocities of the oil samples decreased linearly as the temperature increased.

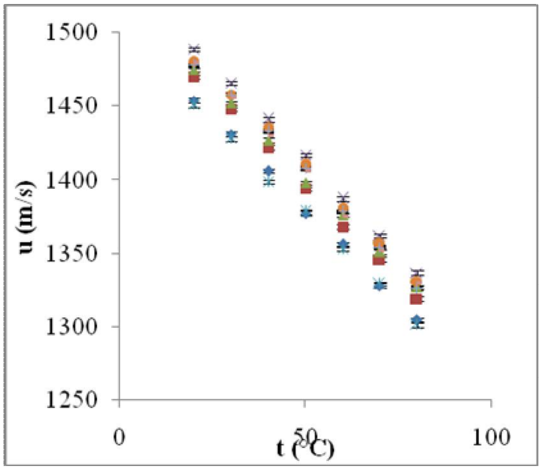

Fig. 3. Ultrasonic velocity of vegetable oils in function of temperature: corn oil, sunflower oil, squash oil, grape seed oil, sesame oil, olive oil, ground nut oil, peanut oil

The ultrasonic velocities evolution with temperature shows a small change of the ultrasonic velocity with the change of the temperature. The evolution of the ultrasonic velocity with temperature was subjected to linear regression to see its prediction using the eq. 5:

$$u = f + g \cdot T \qquad (5)$$

where u – ultrasonic velocity (m/s), f and g are constants, and T – temperature (°C).
The prediction of the equation 5 is in good agreement with the experimental values. All the oil densities were good predicted using the equation, all the regression coefficients ranged between 0.996-0.998.
The mean relative deviation modulus between the prediction and experimental values and average ranged between 0.014 and 0.031%.
Isentropic compressibility (K_S) has been calculated from the equation of Newton LaPlace:

$$K_S = \frac{1}{\rho \cdot u^2} \qquad (6)$$

where ρ – density (kg/m^3) and u ultrasonic velocity in oils.
The isentropic compressibility evolution of oil samples is presented in figure 4.
The isentropic compressibility is increasing with the temperature. The evolution of the K_S with temperature was fitted using a polynomial model (eq. 7):

$$K_S = h \cdot T^2 + i \cdot T + j \qquad (7)$$

where K_S – isentropic compressibility (Pa^{-1}), h, i, and j are constants, and T – temperature (°C).

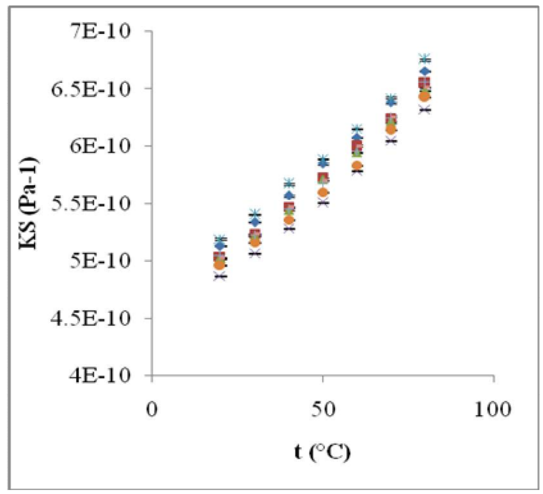

Fig. 4. Isentropic compressibility (K_S) of vegetable oils in function of temperature: corn oil, sunflower oil, squash oil, grape seed oil, sesame oil, olive oil, ground nut oil, peanut oil

The prediction of the equation 15 is in good agreement with the experimental values. All the oils' isentropic compressibility were good predicted using this equation, all the regression coefficients were 0.999. The parameters of equation 15 are presented in table 1.
The intermolecular free length (L_F) is determined using the Jacobson's relation:

$$L_F = \frac{K}{u \cdot \rho^{0.5}} \qquad (8)$$

where K is the temperature Jacobson's constant given by the relation
$K = (90.875+0.375)\cdot 10^{-8}$.

The intemolecular free lenght of oil evolution with temperature is presented in figure 5.

Table 1

Correlation coefficients between isentropic compressibility and temperature

	h	***i***	***j***	**R^2**	**D%**
Corn oil	$7.14\cdot10^{-15}$	$1.85\cdot10^{-12}$	$4.72\cdot10^{-10}$	0.999	0.010
Sunflower oil	$6.90\cdot10^{-15}$	$1.83\cdot10^{-12}$	$4.63\cdot10^{-10}$	0.999	0.009
Squash oil	$5.59\cdot10^{-15}$	$1.90\cdot10^{-12}$	$4.60\cdot10^{-10}$	0.999	0.013
Grape seed oil	$8.92\cdot10^{-15}$	$1.53\cdot10^{-12}$	$4.53\cdot10^{-10}$	0.999	0.012
Sesame oil	$8.33\cdot10^{-15}$	$1.76\cdot10^{-12}$	$4.80\cdot10^{-10}$	0.999	0.015
Olive oil	$4.68\cdot10^{-10}$	$1.20\cdot10^{-12}$	$1.22\cdot10^{-14}$	0.999	0.016
Ground nut oil	$1.26\cdot10^{-14}$	$1.26\cdot10^{-12}$	$4.74\cdot10^{-10}$	0.999	0.014
Peanut oil	$6.07\cdot10^{-15}$	$1.91\cdot10^{-12}$	$4.61\cdot10^{-10}$	0.999	0.010

The experimental data were fitted to the equation 9:

$$L_F = k \cdot T^2 + l \cdot T + m \qquad (9)$$

where L_F is the intermolecular free length of oils (m), k, l and m are fitting parameters, and T is the temperature (ºC). The regression fitting parameters and regression coefficients are presented in table 2. The regression coefficients are closed to 1 for all the oil samples.

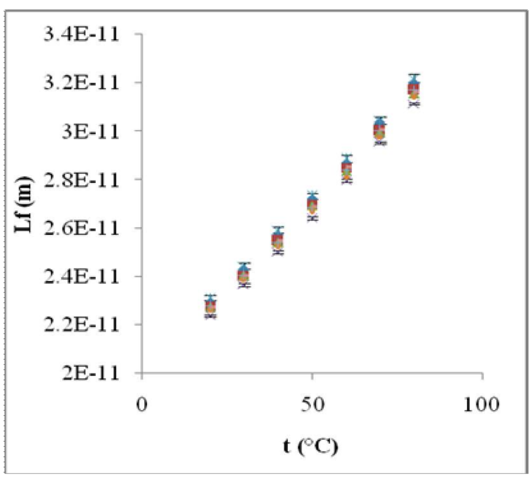

Fig. 5. Intermolecular free length of vegetable oils in function of temperature: ◆ corn oil, ■ sunflower oil, ▲ squash oil, × grape seed oil, ✱ sesame oil, ● olive oil, + ground nut oil, ▬ peanut oil

The specific impedance (Z) is given by the formula:

$$Z = u \cdot \rho \qquad (10)$$

In Figure 6 is presented the specific impedance of oils in function of temperature. The parameters is sensitive with the increasing of the temperature.

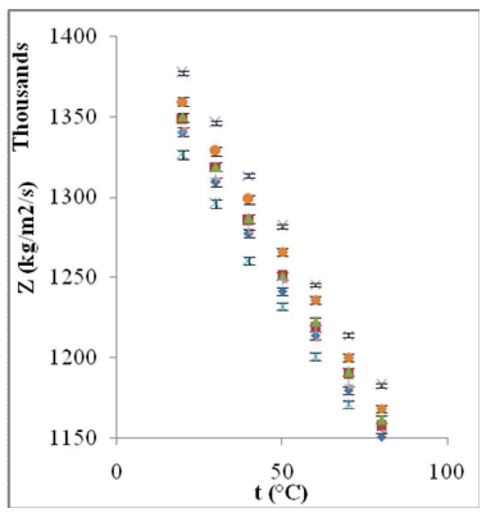

Fig. 6. The specific impedance (Z) of vegetable oils in function of temperature: ◆ corn oil, ■ sunflower oil, ▲ squash oil, × grape seed oil, ✱ sesame oil, ● olive oil, + ground nut oil, ▬ peanut oil

It appears that the evolution of the impedance can be fitted to an linear model:

$$Z = n \cdot T + o \qquad (11)$$

Where Z is the specific impedance ($Kg/m^2/s$), n and o fitting parameters, T – is the temperature (ºC).
The regression coefficients are closed to 1 (table 3), while the relative deviation modulus between the prediction and experimental values and average ranged between 0.564 – 1.821%.

Table 2

Correlation coefficients between intermolecular free length and temperature

Oil	*k*	*l*	*m*	R^2	D%
Corn oil	$3.57\cdot 10^{-16}$	$1.15\cdot 10^{-13}$	$2.05\cdot 10^{-11}$	0.999	0.010
Sunflower oil	$2.97\cdot 10^{-16}$	$1.18\cdot 10^{-13}$	$2.03\cdot 10^{-11}$	0.999	0.009
Squash oil	$2.97\cdot 10^{-16}$	$1.18\cdot 10^{-13}$	$2.02\cdot 10^{-11}$	0.999	0.012
Grape seed oil	$4.04\cdot 10^{-16}$	$1.06\cdot 10^{-13}$	$2.01\cdot 10^{-11}$	0.999	0.008
Sesame oil	$3.45\cdot 10^{-16}$	$1.17\cdot 10^{-13}$	$2.06\cdot 10^{-11}$	0.999	0.013
Olive oil	$3.92\cdot 10^{-16}$	$1.07\cdot 10^{-13}$	$2.03\cdot 10^{-11}$	0.999	0.011
Ground nut oil	$4.16\cdot 10^{-16}$	$1.07\cdot 10^{-13}$	$2.04\cdot 10^{-11}$	0.999	0.012
Peanut oil	$2.26\cdot 10^{-16}$	$1.26\cdot 10^{-13}$	$2.00\cdot 10^{-11}$	0.999	0.008

Table 3

Correlation coefficients between specific impedance and temperature

	n	*o*	R^2	D%
Corn oil	$1\cdot 10^6$	-3193	0,999	1.012
Sunflower oil	$1\cdot 10^6$	-3213	0,999	1.556
Squash oil	$1\cdot 10^6$	-3164	0,999	0.978
Grape seed oil	$1\cdot 10^6$	-3275	0,999	1.245
Sesame oil	$1\cdot 10^6$	-3136	0,999	1.782
Olive oil	$1\cdot 10^6$	-3191	0,999	1.821
Ground nut oil	$1\cdot 10^6$	-3197	0,999	0.564
Peanut oil	$1\cdot 10^6$	-3190	0,999	1.249

Rao's molar sound function (R) [6] was calculated with the expression:

$$R = \frac{u^{\frac{1}{3}}}{\rho} \quad (12)$$

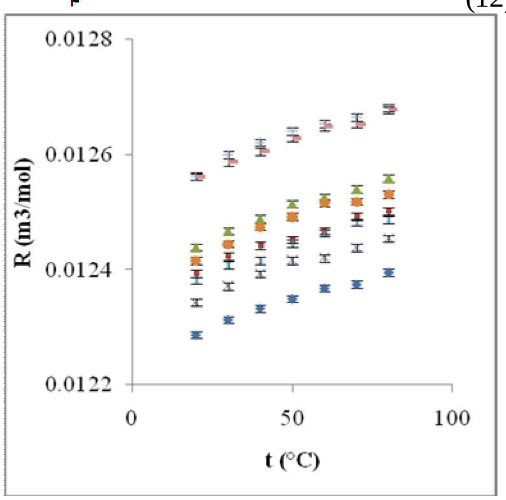

Fig. 7. Rao's molar sound function of vegetable oils in function of temperature: corn oil, sunflower oil, squash oil, grape seed oil, sesame oil, olive oil, ground nut oil, peanut oil

The evolution of Rao´s molar sound is presented in figure 7. The parameter is temperature dependent, is increasing with the increasing of the temperature.
The experimental data were fitted to the equation13:

$$R = p\cdot T^2 + r\cdot T + s \quad (13)$$

Where R – Rao´s molar sound function of oils (m^3/mol), p, r and s are fitting parameters and T is the temperature (ºC).
In table 4 are presented the parameters of equation 13. The regression coefficients ranged between 0.985 and 0.994, while the relative deviation modulus between the prediction and experimental values and average ranged between 0.012 – 0.078 %.
Effect of temperature on surface tension.
The oil's surface tension (computed using the Auerbach relation) ranged between 0.0259 – 0.0334 N/m. A linear evolution of the surface tension evolution with temperature was

observed (fig. 7). The evolution of the surface tension with temperature was subjected to linear regression to see its prediction using the eq. 14:

$$\sigma = x + y \cdot T \qquad (14)$$

where σ – surface tension in N/m, x and y are constants, and T – temperature (°C).

Table 4

Correlation coefficients between Rao´s molar sound function and temperature

Oil	p	r	s	R^2	D%
Corn oil	$-1.151\cdot10^{-8}$	$2.881\cdot10^{-6}$	0.012	0.994	0.012
Sunflower oil	$-6.781\cdot10^{-9}$	$2.422\cdot10^{-6}$	0.012	0.985	0.056
Squash oil	$-1.311\cdot10^{-8}$	$3.249\cdot10^{-6}$	0.012	0.995	0.078
Grape seed oil	$-1.388\cdot10^{-8}$	$3.149\cdot10^{-6}$	0.012	0.989	0.045
Sesame oil	$-9.536\cdot10^{-9}$	$2.781\cdot10^{-6}$	0.012	0.985	0.082
Olive oil	$-2.382\cdot10^{-8}$	$4.295\cdot10^{-6}$	0.012	0.994	0.021
Ground nut oil	$-2.038\cdot10^{-8}$	$3.906\cdot10^{-6}$	0.012	0.993	0.064
Peanut oil	$-9.614\cdot10^{-9}$	$2.829\cdot10^{-6}$	0.013	0.990	0.049

Figure 8 shows that from the relation between surface tension of oil samples and temperature. The relation between the surface tensions of the honey [2] and potassium citrate and its concentration has a similar evolution [7]. All regression coefficients were higher than 0.998.

The values of x ranged between 0.034 and 0.036, while the p was 0.001 for all the oil samples. The mean relative deviation modulus between the prediction and experimental values and average ranged between 0.016 and 0.032%.

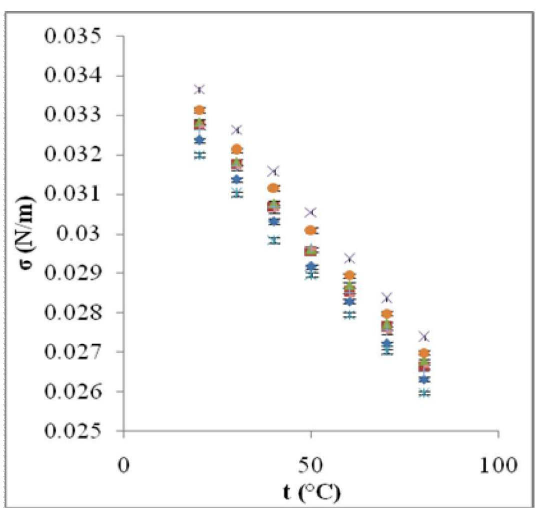

Fig. 8. Surface tension of vegetable oils in function of temperature: corn oil, sunflower oil, squash oil, grape seed oil, sesame oil, olive oil, ground nut oil, peanut oil

Correlations between density, ultrasonic velocity and surface tension

Singh & Singh [8] proposed a linear relation between the ultrasonic velocity, density and surface tension as:

$$\log u = \psi \log \frac{\sigma}{\rho} + \xi \qquad (15)$$

where u – ultrasonic velocity (m/s), σ – surface tension (N/m), ρ - density (kg/m^3), ψ - and ξ - constants.

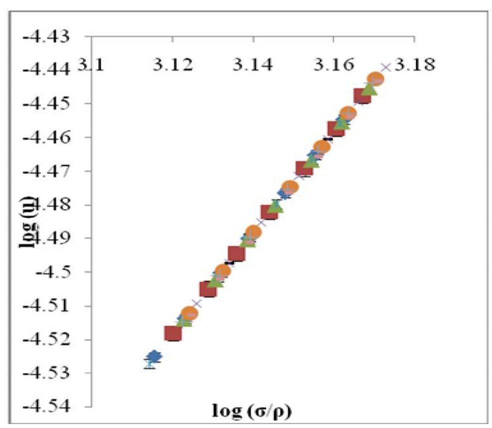

Fig. 9. Correlation between ultrasonic velocity, density and surface tension of vegetable oils: corn oil, sunflower oil, squash oil, grape seed oil, sesame oil, olive oil, ground nut oil, peanut oil

The experimental data of oils (density, viscosity and surface tension) have been subjected to linear regression to assess the applicability of the equation and to compute the two constants. The ultrasonic velocity ($\log u$) - density and surface tension ($\log \frac{\sigma}{\rho}$) for all the oil samples analyzed are plotted in figure 9; it can be observed that the evolution of parameters is a linear one (the regression coefficients is $R^2 = 0.996$), $\psi = 1.500$ and $\xi = -9.198$.

The equation is a perfect tool for predicting the correlation of the three parameters irrespective of the oil origin.

Correlation between surface tension and viscosity

The surface tension and the viscosity are two important properties from the thermophysical point of view for bulk, binary and ternary mixtures of polar and non polar liquids. However, it is interesting to correlate two important thermophysical properties (surface tension and viscosity) of oils so that we can enhance our knowledge about functional dependence of thermophysical properties. For the correlation between surface tension and viscosity we checked the fitness of the experimental values with 4 models: Pelofsky model, a modified Pelofsky model, an exponential model and a polynomial model.

Pelofsky [3] proposed a linear relationship between surface tension and viscosity as:

$$\ln \sigma = \ln A + \frac{B}{\eta} \qquad (16)$$

where σ – surface tension (N/m), lnA and B are fitting coefficients and η – viscosity (Pa·s).

Table 5

Correlation coefficients between surface tension and viscosity according Pelofsky model

Oil	lnA	B	R^2	D%
Corn oil	-3.390	-0.001	0.972	0.176
Sunflower oil	-3.386	0.001	0.984	0.105
Squash oil	-3.397	0.001	0.962	0.101
Grape seed oil	-3.367	0.001	0.971	0.070
Sesame oil	-3.423	0.001	0.966	0.074
Olive oil	-3.388	0.001	0.965	0.089
Ground nut oil	-3.401	0.001	0.972	0.056
Peanut oil	-3.406	0.001	0.953	0.094

In table 5 are presented the fitting coefficients, regression coefficients and the mean relative deviation modulus.

The regression coefficients ranged between 0.953 and 0.984, while the mean relative deviation modulus ranged between 0.056 and 0.176%.

We propose that the surface tension and viscosity of oil samples can be fitted using an modified Pelofsky model as it is presented in equation 17:

$$\ln \sigma = \ln C + D\left(\frac{1}{\eta}\right)^{\Phi} \qquad (17)$$

where ln C and D are substance dependent constants, independent of the thermodynamic state of the system, and Φ is the universal exponent. The exponent Φ = 0.30 is used in eq. 17 to fit the experimental viscosity and surface tension data of oil samples. The characteristic exponent Φ conveniently linearises the plots of ln σ versus oil viscosity, as well as providing the best fit with high accuracy. Figure 10 presents the correlation between the ln σ and $\eta^{-0.3}$, it can be observed the linearised form of the correlation between the two parameters.

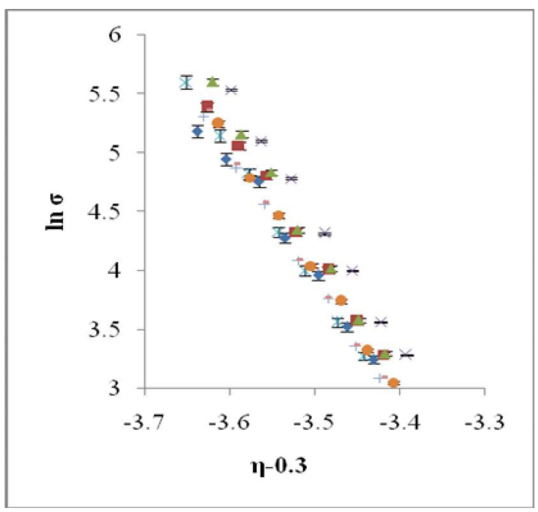

Fig. 10. Correlation between surface tension and viscosity- modified Pelofsky model: corn oil, sunflower oil, squash oil, grape seed oil, sesame oil, olive oil, ground nut oil, peanut oil

Table 6 presents the parameters of the equations 17; it can be observed that the regression coefficients (R^2) are close to 1.

Table 6
Correlation coefficients between surface tension and viscosity according to modified Pelofsky model

	lnC	D	R^2	D%
Corn oil	-3.099	-0.102	0.985	0.166
Sunflower oil	-3.103	-0.096	0.996	0.099
Squash oil	-3.132	-0.087	0.997	0.095
Grape seed oil	-3.093	-0.091	0.999	0.066
Sesame oil	-3.158	-0.088	0.998	0.070
Olive oil	-3.124	-0.094	0.998	0.084
Ground nut oil	-3.136	-0.093	0.999	0.053
Peanut oil	-3.145	-0.091	0.997	0.089

4. Conclusions

The influence of the temperature upon the physical properties of vegetable oils has been achieved at 20 – 80 ºC.

The temperature decreased almost all the physical properties of vegetable oils (exception isentropic compressibility and Rao´s molar sound function). A very good regression coefficients (R^2 = 0.996) was observed between the density, ultrasonic velocity and surface tension.

The modified Pelofsky model predict better than exponential, polynomial and Pelofsky models the correlation between surface tension and viscosity.

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