THERMODYNAMIC CHARACTERIZATION OF A COLLECTION OF OILS OF NUTRITIONAL AND COSMETIC APPLICATION: *Bertholletia excelsa*, *Cocos nucifera*, AND *Pterodon emarginatus Vogel* OILS

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Abstract: This paper contains the results of a new experimental study of the temperature effect on density and ultrasonic velocity for Brazil nut (*Bertholletia excelsa*), coconut (*Cocos nucifera*) and sucupira (*Pterodon emarginatus Vogel*) oils. Isentropic compressibilities and isobaric expansibilities were computed from the experimental magnitudes, as a function of temperature. The Halvorsen's model (HM), and Collision Factor Theory (CFT) were selected for prediction of these properties, due to their wide range of application and easy computation. An accurate response was observed, despite of the use of several simplifications as molecular group contribution procedures for estimation of theoretical critical points of the fatty acids and the complex nature of the studied fluids.

Keywords: Thermodynamic properties; Vegetable oil; Theoretical model; Estimation; Functional group contribution

CARATERIZAÇÃO TERMODINÂMICA DE UM CONJUNTO DE OLEOS DE INTERESSE NUTRICIONAL E COSMÉTICO: OLEOS DE *Bertholletia excelsa*, *Cocos nucifera*, E *Pterodon emarginatus Vogel*

Resumo: Este trabalho apresenta os resultados de um novo estudo experimental sobre o efeito da temperatura na densidade e na velocidade do som dos óleos de noz do Brasil (*Bertholletia excelsa*), coco (*Cocos nucifera*) e sucupira (*Pterodon emarginatus Vogel*). As propriedades derivadas compressibilidade isentrópica e expansibilidade isobarica foram calculadas a partir dos valores experimentais, como função da temperatura. O método de Halvorsen (HM), e a Teoria do Fator de Colisão (CFT) foram selecionadas para modelar estas propriedades devido a o seu amplo range de aplicação e facilidade de implementação. O uso destes modelos matemáticos apresentou baixos desvios apesar da simplificação introduzida na estimação dos pontos críticos dos ácidos graxos, procedimentos de contribuição molecular de grupos funcionais e a natureza estrutural complexa dos óleos.

Palavras-chave: Propriedades termodinâmicas; Óleo vegetal, Modelo teórico, Estimação, Contribuição por grupos funcionais moleculares

1. INTRODUCTION

Thermodynamic properties and phase equilibria data are the most important parameters required in the design of equipments and processes, as well as, predictions and simulations in food technology. Knowledge of these magnitudes as a function of operation magnitudes is of practical interest to the industrial manufacture of fats and oils. Thermal and mechanical procedures applied for oil industry are close related on their temperature and pressure dependence. In spite of their economic importance, no systematic projects of consistent thermodynamic properties of fats and oils have been developed until now, a relative scarce of data being encountered for these kind of compounds. Different previous published works report data compilations of physical and thermal properties of fats and oils [1-12] but this information is not systematic, it is disperse and many physico-chemical properties have not been studied adequately. Fat and oils are of biological nature and then, neither simple nor one-molecular-structured-around. Their thermodynamic properties are strongly dependent of double bound presence and position into the wide molecular structure, chain length, nature of fatty acids and molecular package of esters into solvents. Among the above indicated thermodynamic properties of solvents, volumetric and ultrasonic magnitudes have proved particularly informative in elucidating the complex molecular interaction into liquid phase, being these values of real core interest for direct industrial applications and theoretical predictive models developing. The oils studied here have in common, besides a growing economic importance, applications in food, medical or cosmetic uses, an enormous potential into emerging areas (nutracetics, phytotherapeutics, etc) and, at the same time, a severe gap in terms of physico-chemical data disposability into open literature.

Fats and oils are made up of triglycerides, three molecules of fatty acids joined to a glycerol molecule. The chain length of the fatty acids and their organization on the glycerol backbone vary greatly, although in most of the edible oils it is with 16 and 18 carbons. Fats and oils are a combination of fatty acids, both saturated and unsaturated. The triacylglycerol molecule is often considered the main chemical structure to develop estimative studies on thermophysical properties of oils. The Rackett equation described as Halvorsen method (HM) was tested for density estimation. This method requires the critical properties of the fatty acids and considers their composition as input. The Collision Factor Theory (CFT) using the Wada method for estimation of ultrasonic velocity of the enclosed fatty acids and evaluation of their collision factors was selected for prediction of ultrasonic velocity. Attending to the obtained results, it should be concluded that the tested models offer accurate results of the studied thermodynamic magnitudes, despite geometrical simplifications and the use of estimated critical magnitudes by the Constantinou-Gani group contribution method.

2. METHODOLOGY

2.1. Materials and measurement devices

The oils (cold pressed quality), supplied by usual local providers, were stored in sun light protected form and constant humidity and temperature in our laboratory. They were analysed to determine their fatty acids compositions, the procedure being described earlier [13-14]. The average molar mass was computed as follows:

$$M_{oil} = 3 \cdot \left(\sum_{i=1}^{N} x_i . M_i \right) + 2 \cdot M_{CH_2} + M_{CH} \qquad (1)$$

being x_i the molar fraction and M_i the molar mass of each fatty acid without a proton, N the number of fatty acid found by analysis and M_{CH_2} and M_{CH} are the molar mass contributions of glyceride molecule residue. The variation in the composition between different samples affects mainly the mono and polyunsaturated fatty acids, the change in molar mass being lower than ±1 g mol^{-1}. The molar mass and fatty acids composition are gathered in Table 1. Densities and ultrasonic velocities were measured with an Anton Paar DSA-5000M vibrational tube densimeter and sound analyser, with a resolution of 10^{-5} gcm^{-3} and 1 ms^{-1}. Apparatus calibration was performed periodically in accordance with vendor instructions using Millipore quality water and ambient air at each temperature. Accuracy in the measurement temperature was better than ±10^{-2} K by means of a temperature control device that applies the Peltier principle to maintain isothermal conditions during the measurements. Earlier works describe the experimental procedure usually applied in our laboratory [13-16]. The experimental and disposable literature data of the oils at 298.15 K are gathered in Table 1.

2.2. Data treatment

The measured physical properties were correlated as a function of temperature using Eq. 2:

$$P = \sum_{i=0}^{N} A_i T^i \quad (2)$$

where P is density (gcm^{-3}) or ultrasonic velocity (ms^{-1}), T is absolute temperature in Kelvin and A_i are fitting parameters. N stands for the extension of the mathematical serie, optimised by means of the Bevington test. The fitting parameters were obtained by the unweighted least squared method applying a fitting Marquardt algorithm. The root mean square deviations were computed using Eq. 3, where z is the value of the property, and n_{DAT} is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} \left(z_{exp} - z_{pred} \right)^2}{n_{DAT}} \right)^{1/2} \quad (3)$$

Fitting parameters of the Eq. 2 and the root mean square deviations (Eq. 3) are gathered in Table 2. In Figures 1a, 1b and 2a, the temperature trend of density, ultrasonic velocity and isentropic compressibility (computed by the Newton-Laplace equation from density and ultrasonic velocity) are gathered. These figures show a diminution of density and ultrasonic velocity when temperature rises, due to a sharp diminution of efficiency in terms of molecular structuration into bulk phase of triacylglycerol. Progressively higher molecular kinetics by rising temperatures and steric hindrance of heavy molecular structures produces a growing difficult of packing molecules. As observed in Figure 1a, different collections of density data for Brazil nut and coconut oil are disposable into open literature. As far as we know, our new data of density of sucupira oil are the first to be published. For Brazil nut oil, the three available collections are those of Ceriani et al., 2008, Gonçalves et al., 2014, and Muniz et al., 2015. Only the first author shows an analysis as a function of temperature (only six experimental points). All of them gather lower values than our experimental measurements, Gonçalves et al., 2014 shows an unrealistic value

(4.5% of deviation from our data) far away the other literature collections. The other references, Ceriani et al., 2008, and Muniz et al., 2015 are slightly lower than our collection (0.5% of deviation), but with similar trend in terms of evolution with temperature. For coconut oil, a higher number of references should be found, but only the first of them gathers values as a function of temperature. Noureddini and Qiu´s works are fully coincident with our experimental data. The other collections show strong deviations from our measurements. Such differences are probably related to the difficult of identifying the origin of raw material for oil production, industrial process applied to obtain the oil and purity grade of the oil used in these earlier studies. No information is gathered in these works if the used oil is of refined or virgin nature, as well as, conservation procedure or possivel applied purification pre-treatments. No values were found into open literature for ultrasonic velocity of these oils, as previously commented upon, our new collections of ultrasonic velocities will be too the first ones to be published. In Figure 1b our experimental data of ultrasonic velocities are gathered. Analogously, ultrasonic velocities show a decreasing trend with rising temperatures, with similar trend for Brazil nut and sucupira oil. It is important to point out as the experimental measurements for coconut oil are presented only at the range 293.15-323.15 K due to the high gelling point of this oil. As expected, the isentropic compressibilities increase when temperature rises for the three oils, due to the inverse relation of this magnitude with density and ultrasonic velocity.

3. RESULTS AND DISCUSSION

3.1 Isobaric compressibility

A frequently applied derived quantity is the temperature dependence of volumetric properties, which is expressed as isobaric expansibility or thermal expansion coefficient (α). The data reported in the literature normally show only values of the thermal expansion coefficients both of pure compounds and its mixtures, showing the relative changes in density, calculated by means of ($-\Delta\rho/\rho$) as a function of temperature, and assuming that α remains constant over the temperature range. As in the case of pure chemicals, α can be computed for these oils by way of the following expression:

$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x} \qquad (4)$$

taking into account the strong temperature dependence of density (Figure 1a). Attending to this relation, in Figure 2b is showed the isobaric expansibility of the Brazil nut (Bertholletia excelsa), coconut (Cocos nucifera) and sucupira (Pterodon emarginatus Vogel) oils. As observed, all of them gather negative values, but only for sucupira oil, the isobaric expansibility diminishes almost linearly. Both other oils show maxima at the studied temperature range (294.15 K for Brazil nut oil and 306.15 K for coconut oil).

3.2 Critical point prediction

Constantinou and Gani developed an advanced group contribution method for critical point estimation of covalent molecules, based on the UNIFAC molecular groups. This procedure allows a second order level of contributions, overcoming the

limitation of traditional group contribution models which cannot distinguish isomers or resonance structures. This method was applied to obtain the critical point of the fatty acids enclosed into the studied oils, and then used into the prediction density method that was indicated above. The observed deviations when compared with database information are really negligible.

3.3 Densities estimation

The physical property packages used in powerful chemical simulators typically rely on generalized equations for predicting properties as a function of temperature, pressure, etc. In the last few years, despite the success developing several procedures of density estimation for pure compounds or mixtures, really, only a few of them may be of practical application and high accuracy for fats and oils. One proposed correlation that holds promise for application to oils is the Rackett equation of state, as well as, the modification by Spencer and Danner, 1972.

Table 1: Molar mass, fatty acids compositions and experimental and literature data of density (gcm^{-3}) and ultrasonic velocity (ms^{-1}) for the studied vegetable oils at 298.15 K

Oil	Molar Mass (gmol^{-1})	Fatty Acids Composition (mass%)	
BRAZIL NUT	876.16	*Palmitic (16:0) 13.0* *Stearic (18:0) 3.3* *Oleic (18:1) 42.3*	*Linoleic (18:2) 37.2* *Linolenic (18:3) 2.8* *Araquídic (20:0) 1.4*
COCONUT	882.38	*Miristic (14:0) 0.1* *Palmitic (16:0) 4.7* *Palmitoleic (16:1) 0.3* *Stearic (18:0) 1.3* *Oleic (18:1) 65.3*	*Linoleic (18:2) 19.2* *Linolenic (18:3) 8.3* *Gadoleic (20:1) 0.7* *Erucic (22:1) 0.1*
SUCUPIRA	878.26	*Palmític (16:0) 5.5* *Stearic (18:0) 2.0* *Oleic (18:1) 15.5* *Linoleic (18:2) 46.0*	*Linolenic (18:3) 30.0* *Araquídic (20:0) 0.7* *Gadoleic (20:1) 0.3*
Oil	Exp. Dens.	Lit. Dens.	Exp. Ultra. Vel.	Lit. Ultra. Vel.
BRAZIL NUT	0.915286	0.91462[a] (293.15 K) 0.876960[b] (293.15 K) 0.911[c]	1449.86	N A
COCONUT	0.919272	0.9107[d] (310.97 K) 0.919-0.937[e] (288.15 K) 0.910[f] (293.15 K) 0.9148[g] (288.15 K) 0.93[h] (293.15 K) 0.909[i] (313.15 K)	1408.81	N A
SUCUPIRA	0.926582	N A	1456.30	N A

[a]Ceriani et al., 2008   [f]Lafont et al., 2015
[b]Gonçalves et al., 2014   [g]Sajjadi et al., 2016
[c]Muniz et al., 2015   [h]Kalam et al., 2016
[d]Noureddini et al., 1992   [i]Qiu et al., 2016
[e]Bailey, 2005

Table 2: Parameters of Eq. 2 for 288.15-323.15 K and the corresponding root mean square deviations (Eq 3).

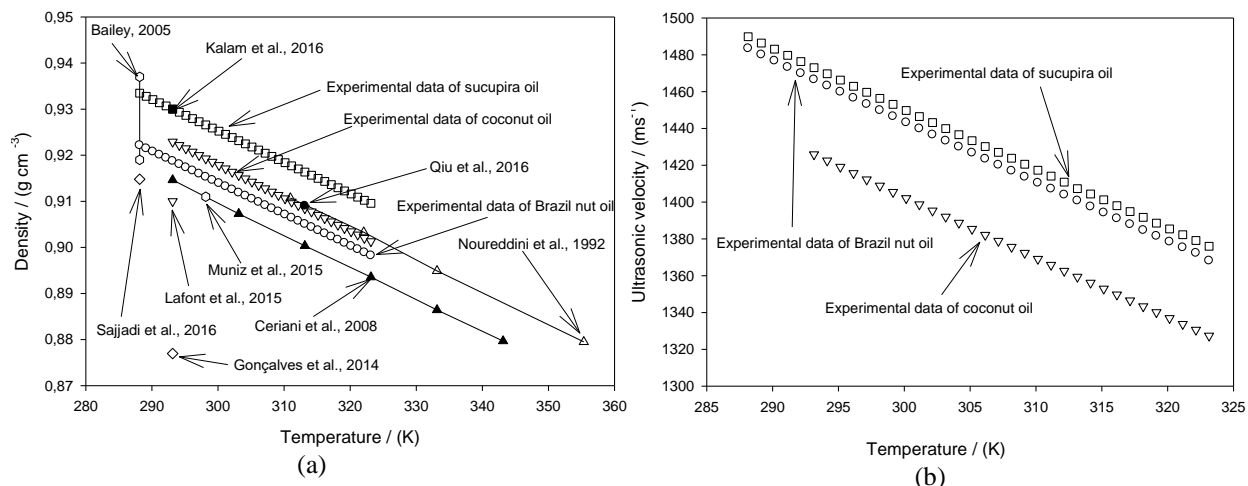|	ρ/(gcm^{-3})					u/(ms^{-1})				
oil	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ
BRAZIL NUT	1.283313	-2.279389e-3	5.162837e-6	-5.560350e-9	1.540e-10	3754.551308	-15.344744	0.036297	-3.608038e-5	9.231e-2
COCONUT	1.225855	-1.533320e-3	2.372553e-6	-2.276184e-9	0.574e-11	5601.527929	-33.106210	0.091952	-9.417774e-5	0.306-2
SUCUPIRA	1.183274	-1.154745e-3	1.382130e-6	-1.330648e-9	0.436e-11	3105.584507	-8.832402	0.014672	-1.207929e-5	2.428e-2

Fig. 1 Dependence of temperature of experimental (a) density and (b) ultrasonic velocity of Brazil nut (*Bertholletia excelsa*), coconut (*Cocos nucifera*) and sucupira (*Pterodon emarginatus Vogel*) oils and available open literature data. Source: The authors themselves.
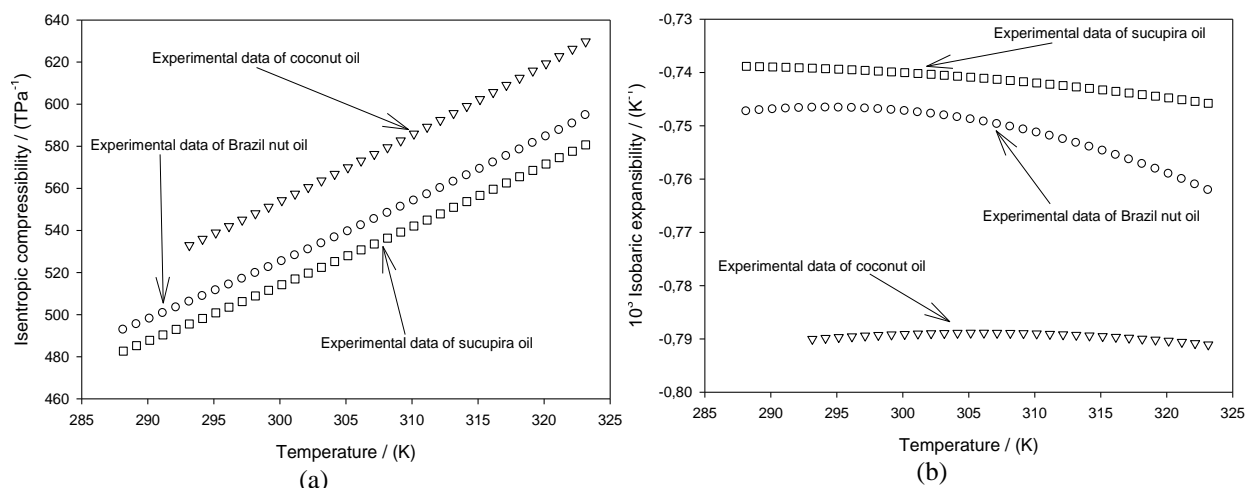

Fig. 2 Dependence of temperature of experimental (a) isentropic compressibility and (b) isobaric expansibility of Brazil nut (*Bertholletia excelsa*), coconut (*Cocos nucifera*) and sucupira (*Pterodon emarginatus Vogel*) oils. Source: The authors themselves.

The procedure proposed by Halvorsen et al. using these equations has demonstrated to be accurate, only requiring critical magnitudes for the enclosed fatty acids and their composition into the oil. If these magnitudes are not known, they must be estimated as indicated above. The procedure of Halvorsen is described as follows:

$$\rho = \frac{\sum x_i \cdot M_i}{R \cdot \left(\dfrac{\sum x_i \cdot T_{ci}}{P_{ci}}\right) \cdot \left(\sum x_i \cdot \beta_i\right)^{[1+(1-T_r)^{2/7}]}} + F_C \quad (5)$$

where ρ is the oil density, x_i is the mole fraction of fatty acids into that oil, M_i is the molar mass of each fatty acid, R is the universal constant of gases, P_{ci} is the critical pressure of each fatty acid and T_r is the reduced temperature. The β parameter is the compressibility factor for the original equation of Rackett (Z_c) or an acentric factor

dependent parameter if we use the modified Rackett equation (Z_{RA}). The Kay´s rule is used to compute the pseudocritical temperature, and F_C is a correction factor proposed by Halvorsen which depends on the oil structure backbone. Table III shows the root square deviations for density values by Halvorsen's model (HM) versus experimental data at 298.15 K.

3.4 Ultrasonic velocities estimation

Ultrasonic velocity has been systematically measured in the last years but this kind of data is extremely scarce yet for fats and oils. The experimental data were compared with the values obtained by the Collision Factor Theory (CFT), which is dependent on the collision factors among molecules as a function of temperature:

$$u = \frac{u_\infty \cdot \left(\sum_{i=1}^{N} (x_i \cdot S_i) \right) \cdot \left(\sum_{i=1}^{N} (x_i \cdot B_i) \right)}{V} \qquad (6)$$

where u_∞ is 1600 m/s, S_i is the collision factor of each fatty acid, Bi is the molecular volume of each fatty acid and V is the molar volume considering each oil a mixture of fatty acids attending to the composition (Table I). The collision factors (Si) were estimated using the Wada method and the molecular volume by Bondi contribution model for each fatty acid. The deviations for CFT method are gathered in Table III.

Table 3: Root mean square deviations (g/cm^3) for Halvorsen model (HM) density prediction and deviations (m/s) for the Collision Factor Theory (CFT) ultrasonic velocity prediction at 298.15 K

oil	Halvorsen model	Collision Factor Theory
BRAZIL NUT	0.015165	3.07
COCONUT	0.053932	3.57
SUCUPIRA	0.023490	5.07

4. CONCLUSION

This paper contains the results of a new experimental study of the effect of temperature on density, and ultrasonic velocity for Brazil nut (Bertholletia excelsa), coconut (Cocos nucifera) and sucupira (Pterodon emarginatus Vogel) oils due to their rising economic importance and potential in emerging areas as nutracetics and phytoterapy. From the experimental investigation and from the above discussions, following conclusions have been drawn:

1. The tested methods Halvorsen's model (HM), and the Collision Factor Theory (CFT)) showed accurate capability of prediction of the measured magnitudes at the range of application, despite of different simplifying assumptions, the use of estimated critical magnitudes by molecular group contribution approach and the complex nature of the studied fluids.
2. A review of physical properties of Brazil nut (*Bertholletia excelsa*), coconut (*Cocos nucifera*) and sucupira (*Pterodon emarginatus Vogel*) oils revealed an important gap in terms of accurate and quality thermodynamic data. The measured experimental collections of density and ultrasonic velocity contribute

for a better characterization of these vegetable oils and increase the disposable data for theoretical works and modelling/simulation of macromolecules.

5. REFERENCES

[1] SINGH, R.P. and D.R. Heldman, "Introduction to food engineering," **Academic Press**, Inc., Orlando, 1984

[2] PRENTICE, J.H. "Measurements in the rheology of food stuffs," **Elsevier Applied Science Pub**. Ltd., Essex, 1984

[3] Le MAGUER, M. and P. Jelen, "Food engineering and process applications," **Elsevier Applied Science Pub**. Ltd., Essex, 1986

[4] RAO, M.A. and S.S.H. Rizvi, "Engineering properties of foods," **Marcel Dekker Inc.,** New York, 1986

[5] LEWIS, M.J. "Physical properties of foods and food processing systems," **Ellis Herwood Ltd.**, Chichester, 1987

[6] Abe, Y. "Handbook of fats and oils," **Saiwai Shobo Co**., Ltd., Tokyo, 1988

[7] WIDLAK, N. "Physical properties of fats, oils and emulsifiers," **AOCS Press**, Champaign, 1999

[8] GUNSTONE, F.D. "Vegetable oils in food technology: composition, properties and uses," **Blackwell Science Ltd**., Oxford, 2002

[9] HELDMAN, D.R., D.B. Lund, and C. Sabliov, "Handbook of food engineering," 2nd ed., **CRC Press**, New York, 2006

[10] SHAFIUR-RAHMAN, M., "Food properties handbook," 2nd ed., **CRC Press**, New York, 2009

[11] MURCOTT*, A., W. Belasco, and P. Jackson, "*The handbook of food research," **Bloomsbury Academic**, New York, 2013

[12] VARZAKAS, T. and C. Tzia, "Food engineering handbook," **CRC Press**, New York, 2014

[13] GONZALEZ, C., J.M. Resa, A. Ruiz, and J.I. Gutierrez, "Densities of mixtures containing n-alkanes with sunflower seed oil at different temperatures," **J. Chem. Eng. Data**, vol. 41, pp. 796-798, 1996

[14] GONZALEZ, C., M. Iglesias, J. Lanz, G. Marino, B. Orge, and J.M. Resa, "Temperature influence on refractive indices and isentropic compressibilities of alcohol (C2-C4)+olive oil mixtures," J**. Food. Eng**., vol. 50, pp. 029-040, 2001

[15] GONZALEZ, C., J.M. Resa, J. Lanz, and M. Iglesias, "Intermolecular interactions in soybean oil+different organic solvents by ultrasonic velocity measurements," **J. Food. Eng**., vol. 77, pp. 152-161, 2006

[16] ANDRADE, R.S., M. Matos, M. Iglesias, and C. Gonzalez, "Temperature influence on thermodynamic properties of argan (Argania spinosa), neem (Azadirachta indica) and common walnut (Juglans regia L.) oils," **Int. J. Eng. Res. Tecnol.,** 5(10), pp. 160-166, 2016.