Thermodynamic Study of Jojoba (Simmondsia Chinensis) Oil as a Function of Temperature

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Abstract— **This paper gathers a new experimental study of the temperature effect on different thermodynamic properties (density, refractive index, dynamic viscosity and ultrasonic velocity) of jojoba (*Simmondsia Chinensis*) oil. Halvorsen's model, Gharagheizi´s group contribution method, Power Law and Collision Factor Theory were selected for prediction of these magnitudes, attending to ease of use and range of application of these thermodynamic magnitudes. Despite different molecular structural simplifications and application of molecular group contribution procedure for theoretical critical point estimation of the studied oil, the experimental thermodynamic data were accurately predicted at different temperatures.**

Keywords—Jojoba oil, Thermodynamic properties, Temperature, Theoretical model

I. INTRODUCTION

Jojoba, with the botanical name Simmondsia chinensis (it is the sole specie of the family Simmondsiaceae), and also known as wild hazel, goat nut, quinine nut, deer nut, pignut, and gray box bush, is native and endemic to Southwestern North America (California, Arizona, Utah (U.S. states) and Baja California (Mexico)). Jojoba is now cultivated in United States, Israel, Mexico, Peru, Australia, India, Egypt, Thailand, South West Africa, Costa Rica, Argentina, Chile and other countries. It has started to gain a lot of importance because of this unusual liquid wax, an ester of long unbranched chain fatty acids and alcohols, in fact, the only liquid wax known to be obtained from the vegetable world. The seeds obtained from the jojoba bush are the source for this liquid, commonly known as "Jojoba Oil". The oil is obtained by pressing the seeds or by extraction with solvents. In the raw state it has a light yellow color. This oil is amazing rare in that it is an extremely long (C_{36}–C_{46}) straight-chain wax ester and not a triglyceride, as it is common. The ester molecule has two double bonds, one at each side of the ester bond. Jojoba oil and its derivative esters are more similar to human sebum and whale oil than to traditional vegetable oils. With virtually no traces of glycerine during industrial processing (hydrogenation, sulfurization, halogenation, sulfurhalogenation, phosphosulfurization, ozonization, hydrolysis, amidation and many other techniques), the importance of jojoba oil in the global market is very high for industries like cosmetic, body-care, pharmaceutical, lubricant and petrochemicals. Jojoba oil is interesting for the industry because it is odorless oil, showing a curious almost temperature-independent viscosity and potential applications varying from lubrication uses to biofuel production [1]. Before developing any industrial application, it is imperative to have accurate and complete information about physico-chemistry and thermodynamic profile of the substances involved. Theoretical models and new procedures for estimation and simulation use experimental collections of thermodynamic data, and in what is referred to fats and oils, an important gap of accurate information is observed into technical and scientific open literature. As a continuation of previous papers related to oils characterization [2-5], we present a study of volumetric, optical, reologic and acoustic properties of jojoba oil. Halvorsen's model [6-7], Gharagheizi´s group contribution method [8], Power Law [9-10] and Collision Factor Theory [11-12] were tested and the obtained results analyzed. These magnitudes were accurately estimated in the studied temperature range, despite molecular structural simplifications into the calculations and the application of molecular group contribution procedures for theoretical critical point estimation of the studied oil.

II. EXPERIMENTAL

A. Materials and measurement devices

The oil was supplied by regional providers (Provital SA, Spain-S.G.S. International Eco Oil Argentina S.A, Argentina, Natural Jojoba Oil FP-35 Golden), and stored in sun light protected form and constant humidity and temperature. It was analyzed to determine their fatty acids compositions [4]. The average molar mass was computed as follows:

$$M_{oil} = \left(\sum_{i=1}^{N} x_i.M_i\right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.M_i\right)_{Alcohols} \qquad (1)$$

being x_i the molar fraction of fatty acids, y_i the molar fraction of alcohols and M_i the molar mass of each fatty acid without a proton and each alcohol without a OH group. N is the number of fatty acids and P the number of alcohols found by analysis. 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, alcohols/fatty acids composition, thermodynamic profile and open literature data are gathered in Table 1 [13-20]. Densities and ultrasonic velocities were measured with an Anton Paar DSA-48 vibrational tube densimeter and sound analyser, (resolution of 10^{-5} gcm^{-3} and 1 ms^{-1}), with accuracy in temperature better than $\pm 10^{-2}$ K by means of a Peltier control device. Refractive indices were measured with a Mettler RE50 refractometer with an uncertainty of ±0.00005, and temperature was controlled as described above. The dynamic viscosities were measured with an Anton Paar AMV 200 rolling ball viscometer with an accuracy of 0.5%, controlling temperature by a Polyscience 9001 thermal bath. Earlier works describe the experimental procedure usually applied in our laboratory [2-4].

B. Data treatment

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

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

where P is density (gcm^{-3}), refractive index, dynamic viscosity (cP) 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, optimized 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.

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

Fitting parameters (Eq. 2) and the root mean square deviations (Eq. 3) are gathered in Table 1. In Figure 1, the temperature trend of the experimental density is gathered with the disposable literature data [13-20]. This figure shows a diminution of density when temperature rises, due to a strong diminution of the packing efficiency by molecules kinetics, as well as, a growing difficult of packing molecules by steric hindrance into bulk liquid phase. Only the values at 298.15 K of Bagby, 1988, El Bassam, 2010, Hussein et al., 2014 and Abdelfatah et al., 2014 are coincident with our measurements. The other collections of Spencer and List, 1988 and Arya and Khan, 2016, overestimate the jojoba oil density until 333.15 K, offering an almost linear trend at the whole range of temperature. In Figure 2, 3 and 4, the temperature trend of refractive index, dynamic viscosity and ultrasonic velocity are enclosed. As previously commented upon, disposable open literature of refractive index offers divergent values at the same experimental condition. While the experimental collections of Bagby, 1988, Spencer and List, 1988, El Bassam, 2010, and Arya and Khan, 2016, are coincident with our new measurements, previous values of Hussein et al., 2014 are really out of trend for this range of temperature (Figure 2).

TABLE I: Thermodynamic profile of jojoba oil, open literature values, properties correlation parameters and models deviations

Molar mass (gmol^{-1})	653.905	
Fatty Acids Composition (mass%)	Vaccenic (18:1): 1.1 Stearic (18:0): 0.1 Palmitoleic (16:1): 0.2 Behenic (22:0): 0.2 Palmitic (16:0): 1.2 Oleic (18:1): 10.1 Gadoleic (14:0): 71.3 Erucic (22:1): 13.6 Nervonic (24:1): 1.3 Linoleic (18:2): 0.1 Heptadecenoic (17:1): 0.1 Arachidic (10:0): 0.1	
Alcohols Composition (mass %)	Hexadecanol: 0.1 Octadecanol: 0.2 Octadec-11-enol :0.4 Octadec-9-enol: 0.7 Docosanol: 1.0 Tetracos-15-enol: 8.9 Eicos-ll-enol: 43.8 Docos-13-enol: 44.9	
Density (298.15 K) (gcm^{-3})	0.861447 0.84 (Wisniak, 1987) 0.8657 (Baldwin, 1988) 0.863 (El Bassam, 2010) 0.863 (Abdelfatah et al., 2012) 0.860 (Hussein et al., 2014) 0.865705 (Arya et al., 2016)	
Refractive index (298.15 K)	1.46434 1.4650 (Bagby, 1988) 1.4650 (El Bassam, 2010) 1.460 (Hussein et al., 2014) 1.46491 (Arya et al., 2016)	
Dynamic viscosity (298.15 K) (cp)	34.99 58 (Bagby, 1988) 35.97 (Spencer and List, 1988) 50 (Abdelfatah et al., 2014) 35.71 (Arya et al., 2016)	
Ultras. veloc. (298.15 K) (ms^{-1})	1395.11	
Density correlation parameters (Eq. 2)	A_0= -1.778355	A_1= 0.027251
	A_2= -9.182365e-5	A_3= 1.010240e-7
	σ = 4.81188E-07	
Refractive index correlation parameters (Eq. 2)	A_0= 1.480721	A_1= 5.994956e-4
	A_2= -3.298073e-6	A_3= 3.699800e-9
	σ = 3.67700e-6	
Dynamic viscosity correlation parameters (Eq. 2)	A_0= 12334.550748	A_1= -111.902568
	A_2= 0.340018	A_3= -3.45656e-4
	σ = 5.10000e-3	
Ultrasonic velocity correlation parameters (Eq. 2)	A_0= 7195.865767	A_1= -47.105522
	A_2= 0.133443	A_3= -1.34422e-4
	σ = 4.85635e-4	
Deviations of Halvorsen´s model at 288.15-323.15 K	σ = 0.055158	

Deviations of Gharagheizi´s model at 298.15 K	σ = 0.00638
Deviations of Power Law´s model at 288.15-323.15 K	σ = 0.1208
Deviations of Collision Factor Theory at 298.15 K	σ = 151.0302

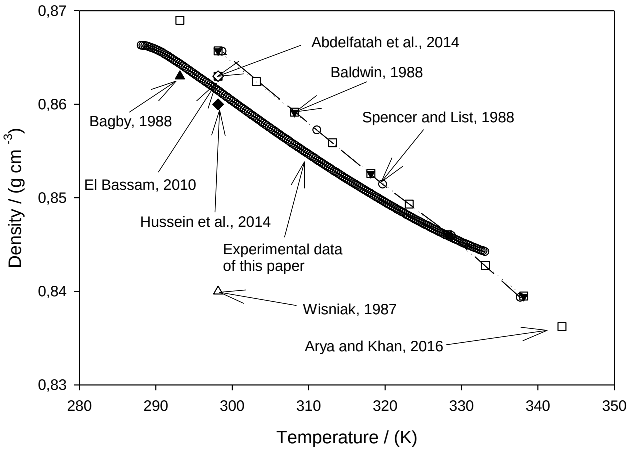

Figure 1: Experimental density and open literature data for jojoba oil

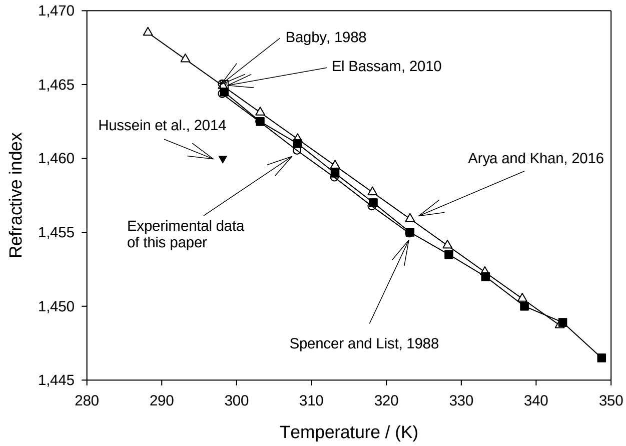

Figure 2: Experimental refractive index and open literature data for jojoba oil

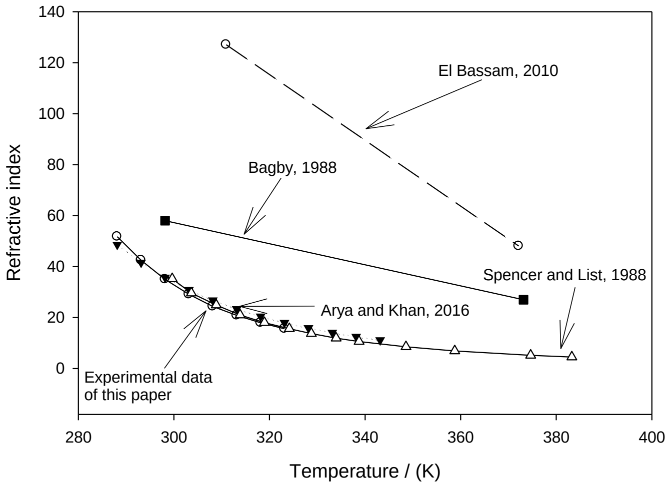

Figure 3: Experimental dynamic viscosity and open literature data for jojoba oil

Analogously, in Figure 3 for dynamic viscosity, the values of Bagby, 1988 or El Bassam, 2010, are completely amazing if compared with the collections of Spencer and List, 1988, Arya and Khan, 2016 or our experimental data, which show clearly the low temperature dependence of jojoba oil dynamic viscosities, as commented in previously published works. In what is referred to ultrasonic velocity for jojoba oil, no available open literature values were found, then our experimental data are the first measurements published, as far as we know. As observed in Figure 4, a decreasing linear tendency was observed for rising temperatures, which is coincident with other previously studied oils [3-4].

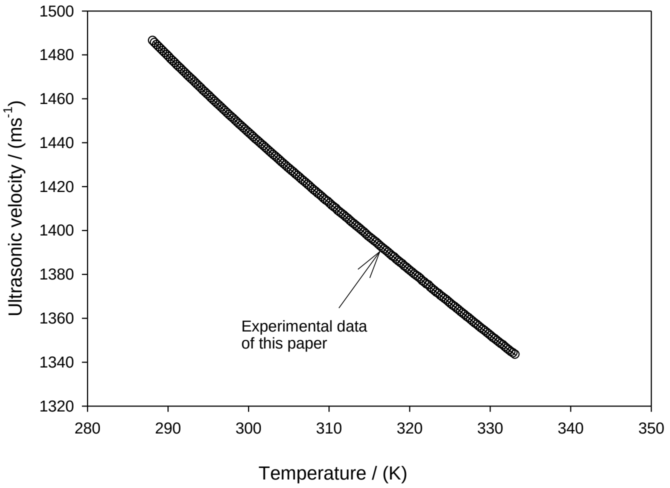

Figure 4: Experimental ultrasonic velocity and open literature data for jojoba oil

C. *Isobaric expansibility*

A frequently applied derived quantity for industrial mixtures is the temperature dependence of volumetric properties, 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 (-Δρ/ρ) as a function of temperature, and assuming that α remains constant over the temperature range. The variable α can be computed by the following equation:

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

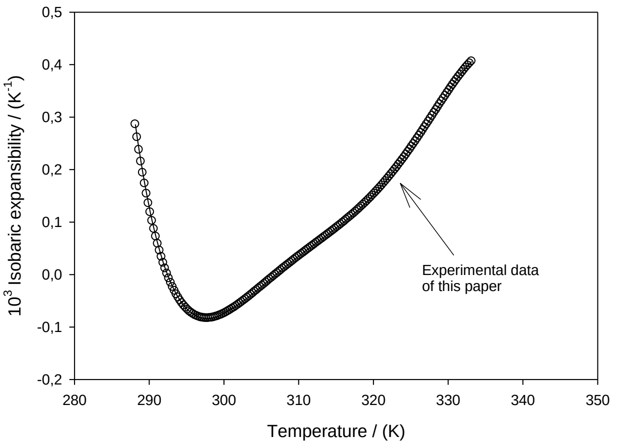

Figure 5 Isobaric expansibility of jojoba oil at different temperatures

Figure 5 shows the isobaric expansibility of the jojoba oil as a function of temperature. As observed, the isobaric expansibility diminishes for rising temperatures from 288.15 K until 297.65 K. From this temperature, the isobaric expansibility rises progressively for increasing temperatures. It is important to highlight as this magnitude reaches negative values around standard condition (from 292.65 to 306.90 K).

TABLE II: Estimated critical properties for the enclosed fatty acids and alcohols into the jojoba oil by Constantinou and Gani method [21]

Fatty acids and alcohols	P_c(MPa)	T_c(K)	Zra
Heptadecenoic	13.484	789.59	0.2267
Palmitic	14.307	780.38	0.2076
Palmitoleic	14.617	781.32	0.2083
Oleic	12.802	797.50	0.1999
Linoleic	13.059	798.36	0.2006
Nervonic	9.0218	838.86	0.1939
Stearic	12.553	796.65	0.1993
Arachidic	11.133	811.57	0.1917
Erucic	10.005	826.09	0.2005
Behenic	0.997	825.36	0.1848
Gadoleic	11.190	812.36	0.2172
Vacenic	12.6373	797.50	0.2142
Hexadecanol	12.876	762.34	0.2093
Octadecanol	12.091	771.51	0.2059
Octadec-11-enol	12.326	772.49	0.2068
Octadec-9-enol	12.326	772.49	0.2068
Docosanol	9.636	804.13	0.1925
Tetracos-15-enol	8.847	819.25	0.1870
Eicos-ll-enol	10.569	819.36	0.2039
Docos-13-enol	9.796	804.95	0.1934

III. MODELING

A. Critical point prediction

The Constantinou and Gani method (CG method) [21] is an advanced group contribution method for critical point estimation, based on the UNIFAC molecular groups. It was applied to obtain the critical point of the fatty acids, and then used into the prediction methods (Table II).

B. Prediction of densities

Despite the success developing different procedures of density estimation, only a few of them may be of real application for fats and oils into food technology. One proposed correlation that holds promise for application to oils is the Rackett equation of state. The modification of this equation by Halvorsen et al. [6-7] has demonstrated to be accurate, only requiring critical magnitudes for the enclosed fatty acids. If these magnitudes are not known, they must be estimated as indicated. The method of Halvorsen is described as follows for jojoba oil:

$$\rho = \frac{\left(\sum_{i=1}^{N} x_i.M_i\right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.M_i\right)_{Alcohols}}{R\cdot\left(\frac{T_{c,oil}}{P_{c,oil}}\right)\cdot\left(Z_{Ra,oil}\right)^{[1+(1-T_r)^{2/7}]}} \qquad (5)$$

where

$$\frac{T_{c,oil}}{P_{c,oil}} = \left(\frac{\left(\sum_{i=1}^{N} x_i.T_{ci}\right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.T_{ci}\right)_{Alcohols}}{\left(\sum_{i=1}^{N} x_i.P_{ci}\right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.P_{ci}\right)_{Alcohols}}\right) \qquad (6)$$

$$Z_{Ra,oil} = \frac{1}{2}\left[\left(\sum_{i=1}^{N} x_i.Z_{Rai}\right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.Z_{Rai}\right)_{Alcohols}\right] \qquad (7)$$

where ρ is the oil density, x_i is the mole fraction of fatty acids and y_i is the mole fraction of alcohols into that oil, M_i is the molar mass of each fatty acid or alcohol, R is the universal constant of gases, P_{ci} is the critical pressure of each fatty acid or alcohol and T_r is the reduced temperature. Z_{Ra} is the Rackett factor of each fatty acid or alcohol [22] (Table II). The mixing rule to compute the pseudocritical temperature, and then the reduced temperature of the oil is described as follows:

$$T_r = \frac{T}{\left(\sum_{i=1}^{N} x_i.T_{ci}\right)_{Fatty\_acids} + \left(\sum_{i=1}^{P} y_i.T_{ci}\right)_{Alcohols}} \qquad (8)$$

C. Prediction of refractive indices

Gharagheizi´s group contribution model was applied for refractive index estimation [8]. This model is, until now, that using the larger database to compute the interaction contributions of the chemical substructures, showing a more robust trend than any other previously tested. Based in 80 chemical structure contributions, the model computes the refractive index using the following equation:

$$n_D = \sum_{i=1}^{80}\left(n_i \cdot n_{Di}\right) + n_{D0} \qquad (9)$$

where n_{D0} and n_{Di} are the intercept of the equation, the contribution of the ith chemical substructure to the refractive index of the compound, and n_i is the number of occurrences of the ith chemical substructure in every chemical structure of the pure compound, respectively.

D. Prediction of dynamic viscosities

The temperature dependence of viscosity of oils should be reasonably described by the Power Law equation [9-10]. The Power Law equation is expressed as:

$$\eta = \eta_0\left(\frac{T - T_x}{T_x}\right)^{-\gamma} \qquad (10)$$

where η is the dynamic viscosity of the oil and T is the absolute temperature. η_0, T_x, and γ are parameters that depend on the reology of the fluid.

E. Prediction of ultrasonic velocities

In terms of fats and oils, ultrasonic measurements are extremely rare. As above indicated, the experimental measurements for ultrasonic velocity enclosed into this paper are the first into open literature. The experimental data were compared with the values obtained by the Collision Factor Theory (CFT) [11-12], which is dependent on the collision factors among molecules as a function of temperature:

$$u = \frac{u_{\infty}.S_{oil}.B_{oil}}{V} \qquad (11)$$

where

$$S_{oil} = \left(\left(\sum_{i=1}^{N} x_i.S_i \right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.S_i \right)_{Alcohols} \right) \qquad (13)$$

$$B_{oil} = \left(\left(\sum_{i=1}^{N} x_i.B_i \right)_{Fatty\_Acids} + \left(\sum_{i=1}^{P} y_i.B_i \right)_{Alcohols} \right) \qquad (14)$$

where u_{∞} is 1600 m/s, S_i is the collision factor of each fatty acid/alcohol, B_i is the molecular volume of each fatty acid/alcohol (calculated by Bondi's method [23]) and V is the molar volume considering the oil, a mixture of fatty acids and alcohols attending to the composition (Table I).

The collision factors (S) were estimated by Eq. 11, using Wada method for estimation of ultrasonic velocity of each fatty acid and alcohol [24]. The deviations for jojoba oil by CFT method are gathered in Table I.

IV. CONCLUSIONS

This paper contains the results of a new experimental study of the effect of temperature on density, refractive index, dynamic viscosity and ultrasonic velocity for jojoba (*Simmondsia Chinensis*) oil. Halvorsen's model for density, Gharagheizi´s group contribution model for refractive index, Power Law for dynamic viscosities and Collision Factor Theory for ultrasonic velocity were selected for prediction of these thermodynamic properties, attending to ease of use and range of application. As a whole, the studied models are, at least, of qualitative accuracy in terms of prediction. Deviations yielded for these thermodynamic magnitudes at the studied range should be considered as a satisfactory result, supporting their validity as predictive tools despite molecular structural simplifications into the calculations and the application of procedures for theoretical critical point estimation of the studied oil.

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