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Mixing properties of (n-alkanes or esters) + olive oil at different temperatures

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Abstract
In the scope of investigating phase equilibria and thermodynamic magnitudes related to equipment design and optimization for edible oil industry, this paper reports refractive index on mixing and ultrasonic velocity of binary systems enclosing a collection of n-alkanes (n-hexane, n-heptane, n-octane, n-nonane), or esters (ethyl acetate, vinyl acetate, propyl acetate, isopropyl acetate, butyl acetate) + olive oil at temperatures from 288.15-298.15 K. From these physical properties, the corresponding derived magnitudes, changes of refractive indices on mixing and change of isentropic compressibilities were computed, being fitted by a modified Redlich-Kister polynomial. Due to the fact of industrial processes design to be strongly computer oriented, consideration was also given to quantify how accurate different theoretical estimation models work. The validity of estimation of these thermodynamic properties was tested by different models, which were selected attending to ease of use, wide range of application and accuracy. From the obtained results we can conclude that an adequate agreement between experimental and computed data, both in magnitude or sign in all range of compositions, was observed.

Keywords. *Refractive index on mixing; isentropic compressibility; n-alkane; ester; olive oil; theoretical model*

1. Introduction

Knowledge of thermodynamic properties of organic substances with edible oils is of main interest for food industry due to the deep impact of physical properties accuracy on final design and optimal improvement of equipments and processes.

Olive oil is associated to high quality gastronomy and a wide number of scientific publications point out its impact as a healthy daily diet component for heart protection. When extracted, this oil contain a number of impurities which have to be removed to make this suitable for human consumption. Removal of this compounds is done in a series of processes, that includes water degumming, chemical or alkali refining, and then bleaching, deodorization and dewaxing. During processing of the olives to obtain the edible oil, different solvents are used to accelerate dewaxing stage, being a main objective of this stage to minimize the quantity of used solvent, as well as, the necessary contact time [1-2]. Optical and ultrasonic mixing properties provide key physicochemical information of liquid food stuffs allowing insight into the structural organization phenomena. Refractive index is an important optical parameter to analyze the light rays traversing through materials medium and can be used as a tool for determinate the adulteration of oils [3-4]. Aditionally, it is known that changes in the refractive indices of fats and oils has a clear relation to rancid odor development [5]. Ultrasonic investigations also found extensive applications in determining the thermodynamic behavior of liquid mixtures [6–11]. Due to its nondestructive nature, ultrasonic study of liquid mixtures has been extensively carried out, and several researchers correlated the experimental results of ultrasonic velocity and the other thermodynamic parameters derived from it (as isentropic compressibilities) with theoretical models and interpreted the results in terms of molecular interactions between the binary liquid mixture components [12–15].

Common physicochemical properties as density or viscosity are available into open literature for edible oils but data are scarce when we talk about refraction or ultrasonic velocity as a function of composition or in terms of mixing properties as a function of temperature or pressure. Continuing previously research [16-20], in this paper, we present new thermodynamic data of refractive indices on mixing and ultrasonic velocities for organic solvent (n-hexane, n-heptane, n-octane, n-nonane, ethyl acetate, vinyl acetate, propyl acetate, isopropyl acetate, butyl acetate) + olive oil mixtures as a function of temperature (283.15-298.15 K). From these magnitudes, derived properties such as change of refractive indices on mixing and changes of isentropic compressibilities were calculated. The computed derived properties were fitted by a modified Redlich-Kister polynomial. Due to the fact of industrial processes design to be strongly computer oriented, consideration was also given to measure how accurate different theoretical estimation models works. The validity of estimation of these thermodynamic properties were tested by different models (a set of empirical equations for refractive index on mixing and the models of Danusso, Nomoto, Junjie, Impedance Model, Collision Factor and Free Length for ultrasonic velocity estimation), which were selected attending to ease of use, range of application and general accuracy. An adequate

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agreement between experimental and computed data, both in magnitude or sign in all range of compositions, was found.

2. Experimental

All the organic solvents used in the preparation of samples were of analytical quality with purity better than 99 mol% (Merk Lichrosolv). Olive oil was supplied by Koipe (Jaén, Spain), being analyzed by means of a gas chromatograph (Perkin-Elmer model Sigma 3B) equipped with a flame detector. Chromatographic technique and fatty acids chemical procedure analysis were described in previous works [16]. The fatty acids composition obtained was palmitoleic acid, 1.1 %; palmitic acid, 16.1 %; stearic acid, 2.4 %; oleic acid 73.4 %, and linoleic acid, 5.7 %; linolenic acid, 1.3 %. The uncertainty in mol% for these results being better than ±0.1 %. From this composition, the average molar mass of this oil has been computed using the following expression:

$$M_{oil} = 3 \cdot \left(\sum_{i=1}^{NFA} x_i M_i \right) + M_{CH-C-CH} \quad (1)$$

where x_i is the mole fraction and M_i the molar mass of each fatty acid according to the concentration analysis, NFA the number of fatty acid found by analysis and $M_{CH-C-CH}$ is the molar mass contributions of the triglyceride molecule axis fraction without three protons. The computed average molar mass in olive oil samples was 870.16 $g \cdot mol^{-1}$. The change in molar mass is less than ±1 $g \cdot mol^{-1}$. The uncertainties in mole fractions were seen less than ±0.0001 in all concentrations. The main physical properties were measured experimentally for each pure component, and the results are shown together with literature values [21-25] in Table 1. GLC tests on the solvents showed solvent purities of higher quality than vendor specifications. The samples were prepared by mass using a Salter ER-182A balance with an accuracy of 5 10^{-4} g, covering the whole composition ranges of the mixtures. A PolyScience controlled bath model 9510 with a temperature stability of $\pm 10^{-2}$ K was used to thermostatize the samples, that stay at the measurement temperature at least one hour before experimental measurements.

The refractive indices were measured by the automatic refractometer ABBEMAT-HP Dr. Kernchen with an uncertainty of ±0.00002. The light source is a light emitting diode (LED) whose beam passes through a polarizing filter, an interference filter (589.3 nm) and various lenses before it passes through the sapphire prism and encounters the sample. The reflected light (angle critical angle) is led via a lens to the optical sensor, which records the critical angle. The temperature at the boundary region prism-sample is measured by the embedded sensor.

The densities and ultrasonic velocities of pure components and their mixtures were measured with a density and sound analyzer (Anton Paar DSA-48), with an uncertainty of ±0.00001 gcm^{-3} ms^{-1} and ±1 ms^{-1}, respectively. The ultrasonic cell determines the ultrasonic velocity of mixtures by means of the sing-around technique. Low intensity ultrasound is used in a very wide range of applications in industry. Many of the applications, such as the measure of density and porosity, involve the measurement of ultrasonic velocities or its attenuation. Lynnworth [26] discusses many of these applications. The principle of operation of the sing-around method in this system is that the received pulse triggers another pulse so that a repetitive trigger signal occurs at a rate equal to the reciprocal of the propagation time. The frequency and thus the period between trigger pulses can be very accurately measured and the system is easily automated. However, any timing delays associated with the electronics will show up as errors in the determination of transit time. These electrical delays may be minimized by appropriate signal processing. This system is easily good to 1% (this is dependent upon path length) for absolute measurements, but is several orders of magnitude more accurate when used as a comparison technique. These procedures are of wide application and have been applied successfully for many types of mixtures. The ultrasonic velocity measuring cell was thermostated with a solid state thermostat using Peltier principle. It consists of a cavity, which is laterally bordered by the receiver and transmitter for the ultrasonic pulses. The surfaces of the ultrasonic transmitter and the receiver are made of stainless steel. A cuvette made of teflon forms all other boundaries of the cavity. The samples are filled and emptied through bores in the cuvette. Therefore all wetted parts consist of teflon and stainless steel only. Apparatus calibration was performed periodically, a double fluid reference being used (Millipore quality degassed water and ambient air) in accordance to technical recommendations.

Additional details of the experimental procedure should be found in earlier published papers, as commented above.

Table 1 Molar mass ($gmol^{-1}$) and physical properties (density (gcm^{-3}), refractive index and ultrasonic velocity (ms^{-1})) of the pure chemicals at 298.15 K.

		Density		*Refractive index*		*Ultrasonic velocity*	
	Molar mass	*This work*	*Lit.*[a]	*This work*	*Lit.*[a]	*This work*	*Lit* [b]
n-Hexane	86.177	0.65502	0.65484	1.37222	1.37226	1076.9	1080
n-Heptane	100.204	0.67955	0.67946	1.38512	1.38511	1130.3	1140
n-Octane	114.231	0.6985	0.69862	1.39513	1.39505	1172.2	1172
n- Nonane	128.258	0.71383	0.71375	1.40305	1.40311	1206.3	1208
Ethyl Acetate	88.106	0.8943	0.89280[c]	1.36968	1.371[c]	1139.5	1143[c]
Vinyl Acetate	86.090	0.92565	0.92634	1.39254	1.3934	1115.7	-
Propyl Acetate	102.133	0.88206	0.88230[c]	1.38172	1.384[c]	1165.4	1149[c]
Isopropyl Acetate	102.133	0.86645	0.87020	1.37462	1.375	1103.6	-
Butyl Acetate	116.160	0.87605	0.87560[c]	1.39184	1.393[c]	1190.5	1201[c]
Olive oil	870.16	0.90928	0.909-0.915[d]	1.46703	1.4677-1.4705	1448.3	1448.2[e]

[21], [22], [23], [24], [25]

3. Results and discussion

3.1 Data correlation

The experimental data of the change of refractive indices on mixture of the binary systems solvent + olive oil at temperatures from 288.15 to 298.15 K are presented in Tables 2-3. The measured ultrasonic velocity, the computed isentropic compressibility, and the deviation of this property are shown in Tables 4-5. The deviations of the properties (change of refractive index on mixing and

change of isentropic compressibility) have been calculated by the following equation:

Table 2. Experimental refractive indices on mixing and change of refractive indices on mixing for n-alkane + olive oil mixtures at 288.15, 293.15 and 298.15 K.

x_1	n_D			δn_D		
	298.15	293.15	288.15	298.15	293.15	288.15
n-Hexane + Olive Oil						
0.0481	1.46072	1.46283	1.46459	0.0040	0.0042	0.0040
0.1022	1.46012	1.46204	1.46392	0.0086	0.0087	0.0085
0.1427	1.45956	1.46144	1.46333	0.0120	0.0120	0.0118
0.1898	1.45882	1.46081	1.46271	0.0159	0.0159	0.0156
0.2685	1.45746	1.45945	1.46139	0.0222	0.0221	0.0218
0.3216	1.45647	1.45835	1.46017	0.0263	0.0262	0.0257
0.3546	1.45558	1.45745	1.45940	0.0287	0.0284	0.0281
0.3998	1.45442	1.45633	1.45828	0.0319	0.0317	0.0313
0.4482	1.45317	1.45483	1.45694	0.0353	0.0349	0.0345
0.5009	1.45127	1.45312	1.45507	0.0386	0.0382	0.0377
0.5505	1.44953	1.45137	1.45348	0.0417	0.0413	0.0409
0.6177	1.44580	1.44787	1.44993	0.0445	0.0443	0.0437
0.6386	1.44480	1.44690	1.44884	0.0455	0.0453	0.0446
0.6988	1.44090	1.44300	1.44480	0.0475	0.0472	0.0464
0.7490	1.43611	1.43840	1.44030	0.0475	0.0475	0.0466
0.7987	1.43085	1.43308	1.43480	0.0471	0.0469	0.0459
0.8491	1.42289	1.42481	1.42702	0.0441	0.0435	0.0429
0.8994	1.41100	1.41305	1.41575	0.0371	0.0366	0.0365
0.9486	1.39498	1.39683	1.39933	0.0258	0.0252	0.0247
n-Heptane + Olive Oil						
0.0484	1.46650	1.46840	1.47027	0.0034	0.0034	0.0034
0.0860	1.46602	1.46787	1.46979	0.0060	0.0059	0.0059
0.1468	1.46517	1.46704	1.46895	0.0102	0.0100	0.0100
0.1938	1.46445	1.46638	1.46831	0.0133	0.0132	0.0131
0.2438	1.46373	1.46551	1.46745	0.0167	0.0164	0.0163
0.3011	1.46252	1.46440	1.46633	0.0202	0.0199	0.0198
0.3465	1.46154	1.46347	1.46548	0.0229	0.0227	0.0226
0.4016	1.46013	1.46211	1.46402	0.0260	0.0258	0.0255
0.4370	1.45956	1.46110	1.46307	0.0283	0.0277	0.0274
0.5205	1.45673	1.45846	1.46035	0.0323	0.0318	0.0314
0.5647	1.45550	1.45667	1.45890	0.0347	0.0336	0.0335
0.6115	1.45300	1.45445	1.45654	0.0361	0.0352	0.0350
0.6465	1.45119	1.45258	1.45467	0.0371	0.0362	0.0359
0.7081	1.44665	1.44855	1.45083	0.0376	0.0371	0.0370
0.7564	1.44233	1.44465	1.44669	0.0373	0.0372	0.0368
0.7999	1.43811	1.43981	1.44231	0.0366	0.0359	0.0359
0.8508	1.43110	1.43307	1.43542	0.0338	0.0333	0.0331
0.9007	1.42125	1.42345	1.42587	0.0280	0.0277	0.0276
0.9507	1.40709	1.40973	1.41207	0.0179	0.0180	0.0178
n-Octane + Olive Oil						
0.0499	1.46648	1.46835	1.47025	0.0030	0.0030	0.0030
0.0957	1.46592	1.46783	1.46966	0.0058	0.0057	0.0056
0.1481	1.46523	1.46707	1.46899	0.0089	0.0087	0.0087
0.2025	1.46453	1.46622	1.46816	0.0121	0.0117	0.0117
0.2467	1.46359	1.46556	1.46740	0.0143	0.0142	0.0141
0.2923	1.46280	1.46462	1.46656	0.0168	0.0166	0.0164
0.3437	1.46166	1.46355	1.46556	0.0193	0.0191	0.0191
0.4016	1.46029	1.46223	1.46415	0.0221	0.0220	0.0218
0.4855	1.45790	1.46012	1.46207	0.0258	0.0258	0.0256
0.5056	1.45725	1.45935	1.46112	0.0266	0.0265	0.0261
0.5498	1.45567	1.45757	1.45955	0.0282	0.0279	0.0276
0.6116	1.45294	1.45508	1.45692	0.0299	0.0298	0.0294
0.6438	1.45135	1.45333	1.45533	0.0306	0.0303	0.0301
0.7021	1.44780	1.44984	1.45183	0.0312	0.0310	0.0307
0.7484	1.44424	1.44636	1.44841	0.0310	0.0308	0.0305
0.8034	1.43900	1.44120	1.44328	0.0297	0.0296	0.0293
0.8533	1.43275	1.43498	1.43711	0.0271	0.0270	0.0267
0.8971	1.42544	1.42773	1.42993	0.0229	0.0228	0.0226
0.9471	1.41392	1.41601	1.41866	0.0150	0.0147	0.0148
n-Nonane + Olive Oil						
0.0454	1.46656	1.46837	1.47037	0.0024	0.0023	0.0024
0.1026	1.46589	1.46774	1.46961	0.0054	0.0053	0.0053
0.1405	1.46530	1.46717	1.46909	0.0073	0.0072	0.0071
0.1966	1.46450	1.46633	1.46828	0.0100	0.0099	0.0099
0.2527	1.46357	1.46546	1.46731	0.0127	0.0126	0.0124
0.3100	1.46246	1.46438	1.46627	0.0153	0.0151	0.0150
0.3616	1.46133	1.46327	1.46523	0.0174	0.0173	0.0172
0.4165	1.45998	1.46193	1.46388	0.0196	0.0195	0.0193
0.4360	1.45961	1.46145	1.46341	0.0205	0.0202	0.0201
0.5161	1.45709	1.45907	1.46100	0.0231	0.0229	0.0227
0.5502	1.45586	1.45785	1.45983	0.0240	0.0239	0.0237
0.6060	1.45358	1.45560	1.45755	0.0253	0.0252	0.0249
0.6440	1.45180	1.45372	1.45579	0.0260	0.0257	0.0255
0.6909	1.44920	1.45129	1.45317	0.0264	0.0262	0.0259
0.7438	1.44564	1.44765	1.44971	0.0262	0.0260	0.0257
0.7955	1.44117	1.44326	1.44541	0.0250	0.0249	0.0247
0.8521	1.43492	1.43713	1.43926	0.0224	0.0223	0.0221
0.8940	1.42870	1.43110	1.43328	0.0189	0.0190	0.0188
0.9531	1.41700	1.41911	1.42121	0.0110	0.0107	0.0104

$$\delta P = P_{mix} - \sum_{i=1}^{N} x_i P_i \tag{2}$$

In this equation, δP means the deviation of a magnitude P (refractive index, n_D, or isentropic compressibility, κ_S, computed by the Newton-Laplace equation), P_i is the pure solvent magnitude, P_{mix} is the value of a property for a mixture, x_i is the mole fraction, and N is the number of components into the mixture.

In Figures 1-2, the derived properties of the studied systems have been plotted along the mole fraction at 298.15 K. The derived magnitudes of the binary mixtures were fitted using a authors' proposed modification of the Redlich-Kister expression:

$$\delta P_{ij} = x_i x_j \cdot \left(\sum_{p=0}^{S} \left(\sum_{j=0}^{M} B_{pj} T^j \right) \cdot \left(x_i - x_j \right)^p \right) \tag{3}$$

where δP_{ij} is the derived property (change of refractive index on mixing or change of isentropic compressibility), B_{pj} are the fitting parameters obtained by the unweighted least squared method applying a fitting Marquardt algorithm (all the points weighting the same), and S is the degree of the polynomial expansion.

The root mean square deviations were computed using eq. 4, where z is the value of the property, and n_{DAT} is the number of experimental data of each experimental collection. In both studied properties, the applied fitting equation fits accurately to the experimental data, as could be observed in Figure 1.

The fitting parameters are gathered into Table 6, with the corresponding root mean square deviations (σ) expressed by eq. 4.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} \left(z_{exp} - z_{pred} \right)^2}{n_{DAT}} \right)^{1/2} \tag{4}$$

The thermodynamic properties have been measured at three temperatures, 288.15, 293.15 and 298.15 K. In Figure 1, the change of refractive indices on mixing with (n-alkane or ester solvent) mole fraction at 298.15 K, should be observed. Figure 2 shows the change of isentropic compressibilities with (n-alkane or ester) mole fraction at 298.15 K.

Figure 3 gathers the composition/temperature trend for n-hexane and ethyl acetate for both derived properties.

Table 3. Experimental refractive indices and change of refractive index of mixing for esters + olive oil mixtures at 288.15, 293.15 and 298.15 K.

x_1	n_D			δn_D		
	298.15	293.15	288.15	298.15	293.15	288.15
Ethyl Acetate + Olive Oil						
0.0603	1.46636	1.46828	1.46965	0.0052	0.0052	0.0046
0.1185	1.46572	1.46762	1.46935	0.0102	0.0101	0.0099
0.1541	1.46530	1.46711	1.46891	0.0133	0.0131	0.0129
0.2014	1.46455	1.46640	1.46818	0.0171	0.0169	0.0167
0.2478	1.46405	1.46571	1.46743	0.0211	0.0207	0.0204
0.3094	1.46269	1.46460	1.46655	0.0258	0.0255	0.0254
0.3497	1.46187	1.46380	1.46568	0.0289	0.0286	0.0284
0.3962	1.46100	1.46273	1.46460	0.0325	0.0321	0.0318
0.4470	1.45960	1.46148	1.46324	0.0361	0.0357	0.0353
0.4982	1.45794	1.45983	1.46169	0.0394	0.0390	0.0386
0.5326	1.45672	1.45867	1.46049	0.0415	0.0412	0.0407
0.6229	1.45270	1.45473	1.45671	0.0463	0.0459	0.0456
0.6498	1.45128	1.45319	1.45512	0.0475	0.0470	0.0466
0.7133	1.44700	1.44896	1.45087	0.0494	0.0489	0.0484
0.7511	1.44370	1.44580	1.44780	0.0498	0.0494	0.0490
0.8039	1.43788	1.43974	1.44174	0.0491	0.0484	0.0480
0.8506	1.43056	1.43277	1.43487	0.0463	0.0460	0.0456
0.8992	1.42005	1.42215	1.42425	0.0406	0.0400	0.0396
0.9517	1.40140	1.40372	1.40597	0.0270	0.0267	0.0264
Vinyl Acetate + Olive Oil						
0.0688	1.46652	1.46840	1.47029	0.0046	0.0045	0.0045
0.1187	1.46611	1.46796	1.46988	0.0079	0.0078	0.0077
0.1608	1.46567	1.46756	1.46944	0.0106	0.0105	0.0103
0.1854	1.46545	1.46728	1.46920	0.0122	0.0120	0.0119
0.2494	1.46467	1.46653	1.46846	0.0162	0.0159	0.0158
0.3000	1.46398	1.46593	1.46790	0.0193	0.0191	0.0189
0.3468	1.46335	1.46526	1.46714	0.0222	0.0218	0.0215
0.3816	1.46275	1.46468	1.46659	0.0241	0.0238	0.0235
0.4391	1.46170	1.46357	1.46557	0.0274	0.0269	0.0266
0.4951	1.46047	1.46236	1.46435	0.0303	0.0298	0.0295
0.5627	1.45859	1.46046	1.46253	0.0335	0.0329	0.0326
0.6125	1.45692	1.45895	1.46087	0.0355	0.0350	0.0345
0.6558	1.45530	1.45711	1.45922	0.0371	0.0364	0.0360
0.6924	1.45339	1.45540	1.45751	0.0379	0.0374	0.0369
0.7616	1.44903	1.45122	1.45316	0.0387	0.0383	0.0376
0.8063	1.44508	1.44718	1.44940	0.0381	0.0375	0.0371
0.8542	1.43937	1.44169	1.44391	0.0360	0.0355	0.0351
0.9024	1.43101	1.43334	1.43577	0.0312	0.0307	0.0304
0.9491	1.41828	1.42087	1.42340	0.0219	0.0217	0.0215
Propyl Acetate + Olive Oil						
0.0490	1.46650	1.46842	1.47029	0.0037	0.0036	0.0036
0.1143	1.46579	1.46769	1.46942	0.0085	0.0084	0.0082
0.1644	1.46510	1.46701	1.46885	0.0121	0.0120	0.0119
0.1946	1.46468	1.46657	1.46852	0.0143	0.0141	0.0141
0.2645	1.46349	1.46543	1.46727	0.0190	0.0189	0.0187
0.3010	1.46282	1.46468	1.46688	0.0215	0.0212	0.0214
0.3542	1.46175	1.46361	1.46567	0.0249	0.0247	0.0246
0.4183	1.46024	1.46214	1.46407	0.0289	0.0286	0.0284
0.4364	1.45973	1.46170	1.46362	0.0299	0.0297	0.0295
0.4897	1.45834	1.46010	1.46206	0.0331	0.0326	0.0324
0.5301	1.45680	1.45887	1.46069	0.0350	0.0348	0.0344
0.5904	1.45428	1.45640	1.45831	0.0376	0.0375	0.0371
0.6386	1.45198	1.45401	1.45599	0.0394	0.0392	0.0388
0.7207	1.44691	1.44879	1.45106	0.0414	0.0409	0.0408
0.7577	1.44355	1.44573	1.44771	0.0412	0.0410	0.0406
0.8054	1.43855	1.44063	1.44282	0.0402	0.0399	0.0397
0.8614	1.43026	1.43240	1.43467	0.0367	0.0364	0.0362
0.9013	1.42211	1.42440	1.42669	0.0320	0.0318	0.0316
0.9551	1.40544	1.40789	1.41021	0.0199	0.0199	0.0196
Isopropyl Acetate + Olive Oil						
0.0543	1.46640	1.46831	1.47020	0.0044	0.0044	0.0043
0.1005	1.46583	1.46772	1.46960	0.0081	0.0080	0.0079
0.1426	1.46542	1.46711	1.46913	0.0116	0.0112	0.0113
0.2007	1.46430	1.46631	1.46816	0.0158	0.0158	0.0156
0.2342	1.46389	1.46569	1.46757	0.0185	0.0182	0.0181
0.2985	1.46251	1.46446	1.46645	0.0231	0.0229	0.0228
0.3537	1.46137	1.46355	1.46514	0.0270	0.0270	0.0265
0.4169	1.45963	1.46183	1.46372	0.0311	0.0311	0.0308
0.4440	1.45894	1.46082	1.46278	0.0329	0.0326	0.0323
0.5332	1.45581	1.45776	1.45984	0.0380	0.0377	0.0375
0.5669	1.45432	1.45637	1.45831	0.0397	0.0394	0.0390
0.6031	1.45274	1.45489	1.45664	0.0414	0.0412	0.0407
0.6462	1.45035	1.45227	1.45422	0.0430	0.0426	0.0422
0.7113	1.44602	1.44791	1.45007	0.0447	0.0442	0.0439
0.7477	1.44255	1.44456	1.44675	0.0446	0.0441	0.0439
0.8052	1.43604	1.43835	1.44034	0.0434	0.0432	0.0427
0.8484	1.42965	1.43184	1.43402	0.0410	0.0407	0.0403
0.9088	1.41620	1.41856	1.42080	0.0332	0.0329	0.0326
0.9530	1.40121	1.40360	1.40617	0.0222	0.0220	0.0220
Butyl Acetate + Olive Oil						
0.0585	1.46639	1.46831	1.47019	0.0038	0.0037	0.0037
0.0856	1.46596	1.46799	1.46987	0.0054	0.0054	0.0054
0.1379	1.46544	1.46728	1.46924	0.0088	0.0086	0.0087
0.1920	1.46464	1.46655	1.46846	0.0120	0.0119	0.0119
0.2415	1.46390	1.46579	1.46771	0.0150	0.0149	0.0149
0.2877	1.46310	1.46495	1.46688	0.0177	0.0175	0.0175
0.3426	1.46202	1.46387	1.46587	0.0207	0.0205	0.0205
0.3938	1.46081	1.46283	1.46472	0.0234	0.0233	0.0232
0.4523	1.45937	1.46124	1.46325	0.0263	0.0261	0.0260
0.5061	1.45776	1.45969	1.46166	0.0288	0.0285	0.0285
0.5493	1.45625	1.45817	1.46012	0.0305	0.0302	0.0301
0.6015	1.45414	1.45608	1.45804	0.0323	0.0320	0.0319
0.6479	1.45185	1.45381	1.45584	0.0335	0.0332	0.0332
0.6921	1.44927	1.45131	1.45331	0.0343	0.0340	0.0339
0.7552	1.44467	1.44666	1.44872	0.0344	0.0341	0.0340
0.7929	1.44105	1.44313	1.44524	0.0336	0.0334	0.0333
0.8474	1.43444	1.43656	1.43866	0.0311	0.0309	0.0308
0.9080	1.42362	1.42581	1.42799	0.0249	0.0246	0.0246
0.9507	1.41230	1.41459	1.41683	0.0168	0.0166	0.0166

3.2 Physical properties estimation

Due to the strong dependence of design and optimization of chemical processes on computer calculations, the availability of accurate and tested methods is of increasing relevance. In what is referred to estimate the refractive indices on mixing, different rules were applied, which are dependent on the pure values at the studied temperature. The experimental refractive indices on mixing have been compared with those estimated by means of the mixing rules proposed by Lorentz-Lorenz (eq. 5), Dale-Gladstone (eq. 6), Eykman (eq. 7), Arago-Biot (eq. 8) Newton (eq. 9), Oster (eq. 10), Eyring-John (eq. 11), Weiner (eq. 12) and Heller (eq. 13) [27]:

$$\frac{n_D^2-1}{n_D^2+2}=\sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right] \quad (5)$$

$$\frac{n_D^2-1}{n_D^2+2}=\sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right] \quad (6)$$

$$n_D-1=\sum_{i=1}^{N}\left[\phi_i\left(n_{Di}-1\right)\right] \quad (7)$$

$$\frac{n_D^2-1}{n_D^2+0.4}=\sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2-1}{n_{Di}^2+0.4}\right)\right] \quad (8)$$

$$n_D=\sum_{i=1}^{N}\left(\phi_i n_{Di}\right) \quad (9)$$

$$n_D^2-1=\sum_{i=1}^{N}\left[\phi_i\left(n_{Di}^2-1\right)\right] \quad (10)$$

$$\frac{(n_D^2-1)(2n_D^2+1)}{n_D^2}=\sum_{i=1}^{N}\left[\phi_i\frac{(n_{Di}^2-1)(2n_{Di}^2+1)}{n_{Di}^2}\right] \quad (11)$$

and for binary mixtures

$$n_D=n_1\phi_1^2+2(n_1n_2)^{1/2}\phi_1\phi_1+n_2\phi_2^2 \quad (12)$$

$$\frac{n_D^2-n_{D1}^2}{n_D^2+2n_{D1}^2}=\left[\phi_2\frac{n_{D2}^2-n_{D1}^2}{n_{D2}^2+2n_{D1}^2}\right] \quad (13)$$

The results of the comparison with experimental data at 298.15 K appear in the Table 7, in which the root mean square deviations (eq. 4) between experimental and estimated data are shown. A good agreement is observed, appearing the lower deviations for Arago-Biot, Gladstone-Dale, Newton and Oster equations for all studied solvents.

Table 4 Experimental data of ultrasonic velocity, isentropic compressibilities and change of isentropic compressibilities for n-alkane + olive oil mixtures at 288.15, 293.15 and 298.15 K.

	u/m·s^{-1}			κ_s/TPa^{-1}			$\delta\kappa_s$/TPa^{-1}		
x_1	298.15	293.15	288.15	298.15	293.15	288.15	298.15	293.15	288.15
n-Hexane + Olive oil									
0.0470	1445.4	1462.5	1479.3	527.7	513.3	499.9	-34.3	-32.2	-30.0
0.1109	1441.3	1458.2	1475.4	531.9	517.7	503.8	-80.6	-75.4	-70.7
0.2048	1434.3	1451.4	1468.4	539.5	524.9	510.8	-147.5	-138.0	-129.4
0.3153	1423.9	1441.3	1458.1	551.1	535.8	521.5	-223.5	-209.5	-196.0
0.4098	1412.9	1430.1	1447.3	563.7	548.1	533.1	-285.9	-267.5	-250.6
0.4527	1406.8	1424.1	1441.2	570.9	554.9	539.7	-312.6	-292.6	-273.9
0.4998	1399.3	1416.6	1433.8	579.9	563.6	548.0	-341.0	-319.0	-298.6
0.5616	1388.3	1405.6	1423.0	593.4	576.6	560.4	-376.4	-352.0	-329.4
0.5972	1380.1	1397.6	1414.9	603.8	586.4	569.9	-394.3	-368.7	-344.8
0.7010	1348.7	1366.6	1384.2	646.2	626.7	608.4	-434.1	-405.7	-379.0
0.7970	1306.7	1325.9	1343.9	709.6	685.8	664.7	-446.9	-418.0	-389.8
0.9027	1227.3	1246.7	1265.0	857.6	827.0	799.2	-382.6	-355.5	-329.2
0.9493	1153.4	1174.4	1195.1	1042.9	1000.2	960.3	-234.3	-217.0	-200.7
n-Heptane + Olive Oil									
0.0448	1445.6	1462.8	1479.4	527.5	513.0	499.7	-25.2	-23.9	-22.3
0.0964	1442.4	1459.6	1476.2	530.9	516.4	502.9	-54.2	-51.1	-48.0
0.1904	1435.8	1453.0	1469.7	538.1	523.4	509.6	-105.9	-99.6	-94.0
0.3087	1425.5	1442.7	1459.5	549.8	534.7	520.5	-168.4	-158.2	-149.4
0.4090	1414.4	1431.6	1448.5	562.7	547.3	532.4	-218.3	-204.9	-193.7
0.4577	1407.9	1425.1	1442.1	570.6	554.8	539.6	-241.1	-226.2	-213.8
0.4968	1402.0	1419.2	1436.3	577.8	561.7	546.2	-258.3	-242.4	-229.0
0.5463	1393.2	1410.4	1427.6	588.8	572.4	556.4	-278.4	-261.0	-246.6
0.6175	1378.7	1396.1	1413.2	607.6	590.2	573.7	-304.2	-285.2	-269.2
0.7016	1356.3	1374.2	1391.5	638.3	619.3	601.4	-326.2	-305.8	-288.6
0.7922	1320.6	1337.3	1356.1	692.3	673.0	651.1	-329.0	-305.7	-289.6
0.8903	1258.6	1277.6	1296.5	803.7	776.3	750.1	-279.2	-260.3	-245.6
0.9499	1199.6	1220.1	1240.2	937.7	901.9	868.0	-182.6	-170.0	-161.1
n-Octane + Olive Oil									
0.0408	1445.8	1463.8	1478.1	527.1	512.2	501.3	-18.7	-18.3	-14.7
0.1123	1441.7	1458.8	1475.5	531.8	517.4	503.9	-51.0	-48.1	-45.2
0.1931	1436.1	1453.3	1469.9	538.1	523.5	509.7	-86.6	-81.6	-76.9
0.3038	1426.9	1444.1	1460.9	548.7	533.7	519.5	-133.3	-125.6	-118.6
0.4047	1416.3	1433.5	1450.4	561.3	545.9	531.1	-172.9	-162.8	-153.7
0.4554	1409.9	1427.1	1444.1	569.1	553.4	538.3	-191.4	-180.1	-170.1
0.5088	1402.3	1419.4	1436.5	578.7	562.7	547.1	-209.6	-197.0	-186.0
0.5474	1396.1	1413.3	1430.4	586.6	570.3	554.5	-221.6	-208.3	-196.6
0.6000	1386.3	1403.2	1420.8	599.5	583.0	566.3	-236.0	-221.3	-209.2
0.7121	1358.4	1376.0	1393.5	638.4	619.7	601.7	-255.1	-239.6	-225.9
0.8047	1324.4	1341.8	1360.1	691.1	670.9	649.7	-250.3	-233.7	-220.8
0.9090	1263.4	1282.4	1300.4	804.3	777.0	752.0	-191.2	-178.7	-167.0
0.9501	1228.3	1247.2	1266.7	883.8	853.6	822.6	-133.0	-122.1	-115.4
n-Nonane + Olive Oil									
0.0435	1446.0	1464.3	1479.7	527.1	511.6	499.5	-16.6	-17.0	-14.6
0.1183	1441.6	1458.4	1475.5	532.1	517.9	504.0	-44.4	-41.8	-39.6
0.1993	1436.3	1453.1	1470.1	538.2	523.9	509.9	-73.7	-69.5	-65.7
0.3006	1428.1	1444.9	1462.1	547.8	533.2	518.7	-108.4	-102.4	-96.9
0.4048	1417.9	1434.7	1452.0	560.3	545.2	530.1	-141.6	-133.6	-126.5
0.4571	1410.1	1428.2	1445.9	569.5	553.0	537.3	-155.3	-147.6	-140.0
0.5037	1405.2	1422.4	1439.7	576.2	560.2	544.6	-169.0	-159.8	-151.1
0.5525	1397.8	1415.0	1432.4	585.9	569.5	553.5	-180.7	-170.8	-161.4
0.6059	1388.4	1405.6	1423.1	598.5	581.6	565.1	-191.5	-180.8	-170.9
0.7038	1366.2	1383.8	1401.3	629.9	611.5	593.8	-203.0	-191.7	-180.7
0.8017	1335.0	1352.9	1371.0	678.4	657.8	637.8	-197.3	-186.1	-175.4
0.9037	1284.3	1303.3	1322.1	770.8	745.0	720.6	-149.5	-141.2	-132.8
0.9528	1249.9	1269.2	1288.7	846.6	817.0	788.6	-95.3	-89.6	-84.2

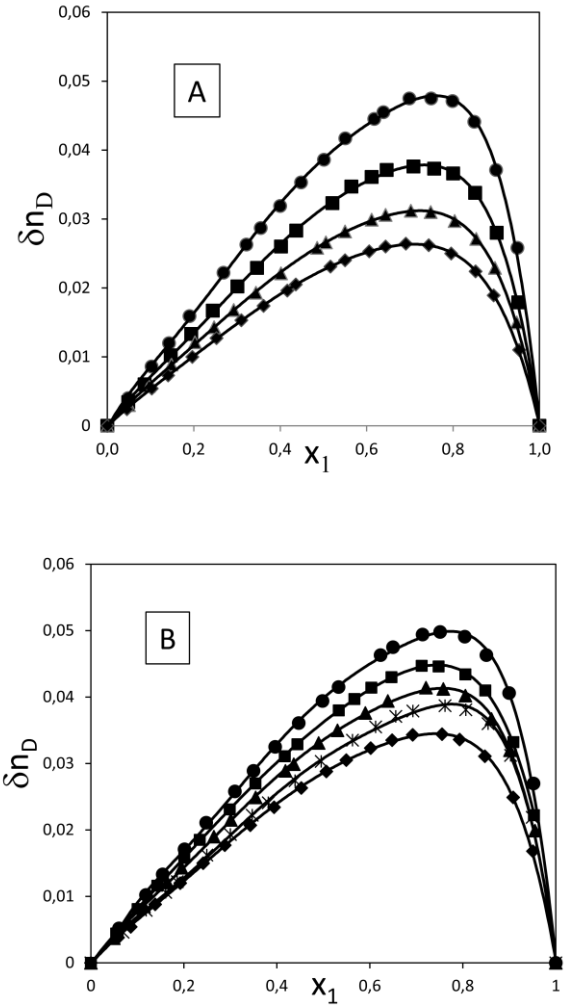


Figure 1. Change of refractive index on mixing versus mole fraction at 298.15 K for (A) (●) n-hexane, (■) n-heptane, (▲) n-octane, (◆) n-nonane) (1)+olive oil (2) and (—, Eq. 3) fitting curves and for (B) ((●) ethyl acetate, (*) vinyl actetate, (▲) propyl acetate, (■) isopropyl acetate, (◆) butyl acetate)(1)+olive oil (2) and (—, Eq. 3) fitting curves

Mixtures containing esters as well as higher molecules (n-nonane, butyl acetate) gather the best results in terms of deviations (Figure 4). Experimental data of mixing ultrasonic velocities were compared to values obtained by the following rules: Danusso (eq. 14) [28], Nomoto (eq. 15) [29], Junjie (eq. 16) [30], Impedance Model (eq. 17) [31], Collision Factor Theory (eq. 18) [32], and Free Length Theory (eq. 19) [33].

$$u=\frac{1}{\rho_{mix}}\left(\frac{1}{M_{eff}}\sum\frac{x_iM_i}{\rho_i^2u_i^2}\right)^{1/2} \quad (14)$$

where M_{eff} is the effective molar mass.

$$u=\left(\sum\frac{x_iR_i}{x_iV_i}\right)^3 \quad (15)$$

where R and V are molar sound velocity and molar volume.

Table 5. Experimental data of ultrasonic velocity, isentropic compressibilities and change of isentropic compressibilities for esters + olive oil mixtures at 288.15, 293.15 and 298.15 K.

	u/m·s^{-1}			κ_s/TPa^{-1}			$\delta\kappa_s$/TPa^{-1}		
x_1	298.15	293.15	288.15	298.15	293.15	288.15	298.15	293.15	288.15
Ethyl Acetate + Olive oil									
0.0466	1446.0	1463.0	1480.6	526.3	512.2	498.2	-14.2	-13.1	-12.3
0.0951	1443.5	1460.5	1477.9	528.1	514.0	500.0	-28.7	-26.4	-24.4
0.1904	1437.8	1454.8	1472.3	532.5	518.1	504.0	-56.4	-52.0	-48.1
0.2997	1430.1	1447.2	1464.5	538.4	523.8	509.5	-87.2	-80.4	-74.2
0.3963	1421.1	1438.4	1455.9	545.5	530.4	515.7	-112.7	-103.9	-95.9
0.4478	1415.3	1432.9	1450.2	550.1	534.6	519.9	-125.3	-115.8	-106.6
0.5007	1408.6	1426.2	1443.7	555.5	539.7	524.7	-137.8	-127.1	-117.1
0.5557	1400.3	1418.1	1435.5	562.3	546.1	530.9	-149.4	-137.9	-126.9
0.6025	1391.9	1409.9	1427.7	569.3	552.6	536.8	-158.2	-145.9	-134.5
0.7022	1368.6	1387.0	1405.0	589.5	571.6	554.7	-171.5	-158.0	-145.4
0.8089	1329.2	1349.2	1368.1	626.2	604.9	585.8	-170.7	-157.9	-145.2
0.8989	1271.6	1291.6	1311.4	686.1	661.8	638.7	-141.1	-129.1	-118.3
0.9519	1215.7	1236.8	1257.9	753.0	723.5	695.6	-92.1	-84.0	-76.8
Vinyl Acetate + Olive Oil									
0.0435	1446.2	1463.1	1480.2	526.0	512.0	498.3	-13.6	-12.4	-11.5
0.1001	1443.2	1460.1	1477.2	528.1	514.0	500.3	-30.9	-28.3	-26.2
0.2079	1436.4	1453.6	1470.2	533.1	518.5	505.0	-62.9	-58.1	-53.3
0.3041	1429.1	1446.4	1463.5	538.4	523.5	509.4	-90.6	-83.7	-77.2
0.3956	1420.3	1437.6	1454.8	544.9	529.9	515.4	-115.5	-106.5	-98.2
0.4418	1415.2	1432.5	1449.7	548.8	533.5	518.9	-127.5	-117.5	-108.3
0.5072	1406.3	1423.8	1441.1	555.6	539.9	524.9	-143.1	-132.0	-121.7
0.5433	1400.1	1417.8	1435.1	560.4	544.3	529.2	-150.7	-139.0	-128.0
0.5973	1390.6	1408.3	1425.7	567.9	551.5	535.9	-161.7	-149.0	-137.2
0.7053	1365.0	1383.1	1400.9	588.9	571.1	554.3	-177.8	-163.7	-150.6
0.7968	1328.0	1347.6	1366.0	621.2	600.6	581.9	-176.9	-163.4	-150.0
0.8972	1260.1	1279.7	1299.3	687.8	663.4	640.4	-144.8	-132.4	-121.2
0.9605	1199.2	1219.9	1240.5	756.7	727.0	699.1	-97.6	-89.0	-81.1
Propyl Acetate + Olive Oil									
0.0451	1446.1	1463.1	1480.9	526.2	512.1	498.0	-12.6	-11.7	-11.1
0.0914	1443.7	1460.8	1477.9	528.1	513.8	500.1	-25.0	-23.2	-21.4
0.1987	1437.4	1454.7	1471.6	533.0	518.4	504.7	-53.4	-49.5	-45.7
0.3039	1429.7	1446.9	1464.1	539.1	524.3	510.1	-80.0	-73.9	-68.6
0.3903	1421.9	1438.9	1456.5	545.4	530.5	515.7	-100.4	-92.5	-86.1
0.4476	1415.6	1432.7	1450.4	550.6	535.4	520.4	-113.0	-104.1	-96.9
0.4963	1409.6	1426.8	1444.5	555.6	540.1	524.9	-123.1	-113.4	-105.5
0.5412	1403.1	1420.5	1438.3	561.0	545.2	529.6	-131.6	-121.2	-112.8
0.6020	1392.8	1410.2	1428.3	569.9	553.6	537.5	-141.6	-130.3	-121.3
0.7001	1370.9	1388.7	1407.0	589.3	571.9	554.8	-152.6	-140.2	-130.4
0.8018	1336.4	1354.2	1373.6	622.1	603.2	583.7	-151.3	-138.2	-128.8
0.9001	1279.7	1298.6	1318.8	682.4	659.5	636.2	-121.5	-110.2	-102.7
0.9517	1231.7	1252.2	1272.7	740.6	712.7	686.3	-79.2	-71.7	-66.5
Isopropyl Acetate + Olive Oil									
0.0489	1445.3	1462.0	1479.4	526.8	512.9	499.1	-18.6	-17.1	-15.8
0.1005	1442.2	1458.7	1476.2	529.3	515.4	501.5	-38.0	-35.0	-32.4
0.2033	1434.6	1451.3	1468.9	535.4	521.1	506.8	-75.4	-69.8	-64.8
0.3035	1425.7	1442.3	1459.8	542.5	528.1	513.6	-110.6	-102.3	-94.8
0.4006	1414.8	1431.6	1449.4	551.6	536.6	521.5	-142.6	-132.1	-122.6
0.4446	1409.0	1425.8	1443.7	556.5	541.3	526.0	-156.3	-144.7	-134.2
0.4946	1401.4	1418.4	1436.3	562.9	547.4	531.7	-171.0	-158.3	-146.8
0.5504	1391.7	1408.7	1426.7	571.5	555.5	539.5	-186.1	-172.2	-159.6
0.5966	1382.2	1399.3	1417.4	579.9	563.6	547.1	-197.1	-182.3	-168.9
0.6947	1356.1	1373.6	1392.0	604.2	586.5	568.7	-214.3	-198.1	-183.3
0.7971	1314.5	1332.6	1351.6	646.3	626.0	605.9	-215.5	-198.9	-183.7
0.8988	1244.2	1263.5	1283.5	728.0	702.5	677.4	-176.8	-162.5	-149.5
0.9558	1178.5	1199.1	1220.2	819.7	787.3	756.1	-109.2	-100.2	-91.8
Butyl Acetate + Olive Oil									
0.0503	1445.8	1462.4	1479.9	526.5	512.7	498.7	-12.5	-11.4	-10.6
0.0995	1443.3	1459.9	1477.5	528.4	514.5	500.5	-24.4	-22.5	-21.0
0.1896	1438.1	1454.8	1472.4	532.6	518.4	504.2	-45.5	-42.3	-39.5
0.3056	1429.9	1446.6	1464.3	539.2	524.8	510.3	-71.4	-66.4	-62.0
0.3939	1422.2	1438.9	1456.6	545.5	530.9	516.1	-89.9	-83.6	-77.9
0.4435	1416.9	1433.8	1451.6	550.0	535.0	520.0	-99.4	-92.5	-86.3
0.4972	1410.5	1427.4	1445.2	555.3	540.2	524.9	-109.0	-101.5	-94.5
0.5603	1401.7	1418.7	1436.6	563.0	547.5	531.8	-119.2	-110.8	-103.3
0.6002	1395.2	1412.1	1430.2	568.7	552.9	536.9	-124.7	-115.8	-108.0
0.6987	1374.5	1391.6	1410.1	587.3	570.7	553.6	-133.6	-124.0	-115.5
0.8108	1338.3	1356.2	1375.0	622.4	603.5	584.6	-130.0	-120.7	-112.2
0.9076	1285.4	1304.1	1323.7	679.7	657.3	635.0	-99.9	-92.4	-85.6
0.9492	1250.5	1269.9	1290.0	722.1	696.7	671.7	-69.2	-64.0	-59.1

$$u = \left(\sum \frac{x_i V_i}{x_i M_i} \right)^{1/2} \left(\sum \frac{x_i V_i}{\rho_i u_i} \right)^{-1/2} \qquad (16)$$

$$u = \left(\frac{\sum x_i Z_i}{\sum x_i \rho_i} \right) \qquad (17)$$

where Z_i is specific acoustic impedance.

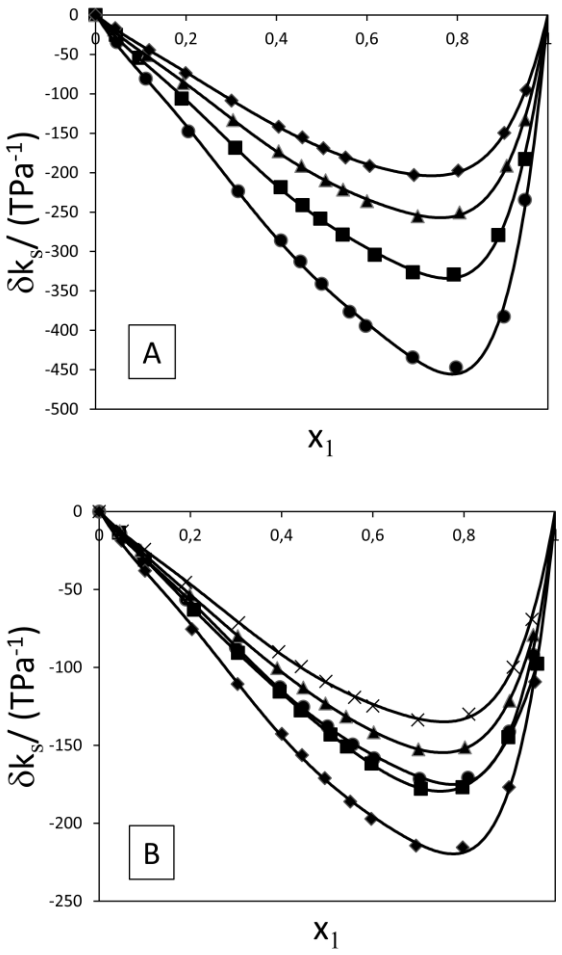


Figure 2. Change of isentropic compressibilities (TPa^{-1}) versus mole fraction at 298.15 K for (A)((●) n-hexane, (■) n-heptane, (▲) n-octane, (◆) n-nonane)(1) + olive oil (2) and (—, Eq. 3) fitting curves and for (B) ((●) ethyl acetate, (*) vinyl actetate, (▲) propyl acetate, (■) isopropyl acetate, (◆) butyl acetate)(1) + olive oil (2) and (—, Eq. 3) fitting curves

The Collision Factor Theory (CFT) is dependent on the collision factors among molecules as a function of temperature into pure solvent or mixture (eq. 18). The collision factors (S) and the characteristic molecular volumes (B) of the pure solvents used in the CFT calculations were estimated by using the experimental ultrasonic velocities, enclosed in this paper, and the corresponding molar volumes from open literature [16-17]. These values could be also evaluated by means a group contribution procedure (Bondi´s group contribution methodology), when no experimental ones are disposable.

$$u = \frac{u_\infty \sum x_i S_i \sum x_i B_i}{V_{mix}} \qquad (18)$$

In this equation, u_∞ is 1600 m/s, S is collision factor, B is volume of molecule per mole and V is molar volume.

The Free Length Theory (FLT) estimates the ultrasonic velocity of a mixture attending to the free displacement of molecules (L_f) as a main function of temperature, then (eq. 19):

$$u = \frac{K}{L_{mix}\rho_{mix}^{1/2}} \tag{19}$$

where

$$L_{mix} = 2\left(\frac{V_{mix} - \sum x_i V_i}{\sum x_i Y_i}\right) \tag{20}$$

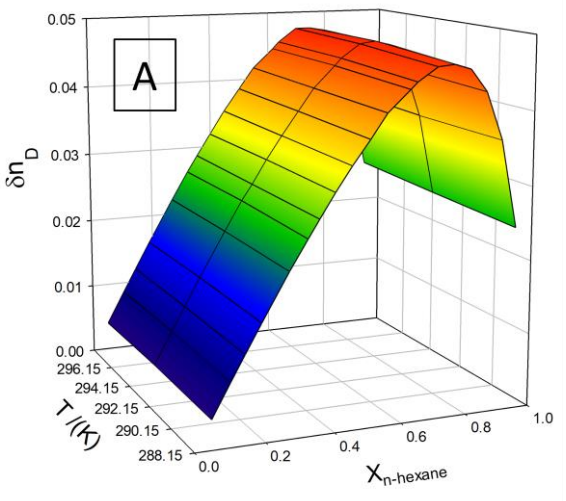
where V_i represent the volume at absolute zero of each pure component and Y_i is the surface area per mole, and is defined as:

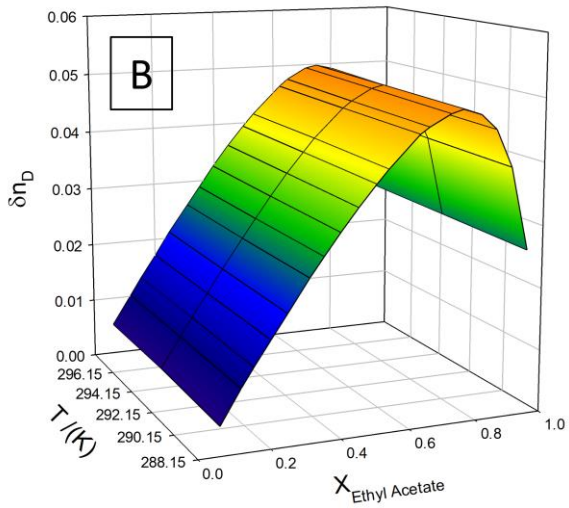
$$Y = \frac{2V_{mix}}{L_{f\,mix}}\left(1 - \frac{u_{\exp}}{u_{\infty}}\right) \tag{21}$$

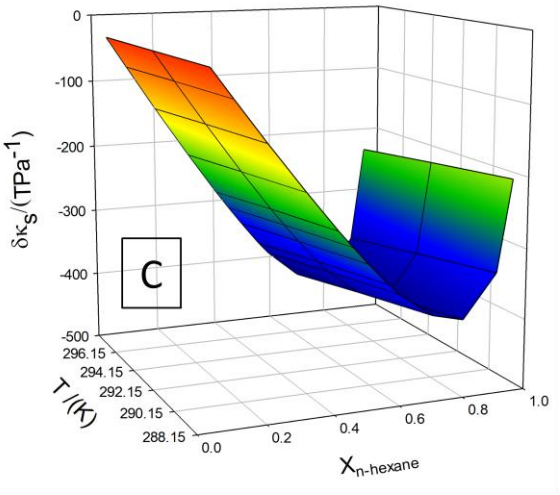
The pertinent relations in these theories, as well as, their theoretical basis were described at the literature cited.

4. Discussion and conclusions

Although the mixing properties behaviour as a function of temperature or pressure has been investigated in the last few years, most studies have been related to liquid mixtures containing light molecules, biological macromolecules has hitherto received comparatively little attention. This fact is really amazing attending to its key role in food industry or biotechnology processes. In spite of much investigation, however, the exact nature of solvation procedure of macromolecules in short solvents, as triglycerides in n-alkane or ester solvents, remains a little bit obscure. Up to the present, little attention has been paid to thermodynamic studies in edible oil mixtures with potential separation solvents by environment friendly procedures of extraction, and refining such as modified distillation or wintering.







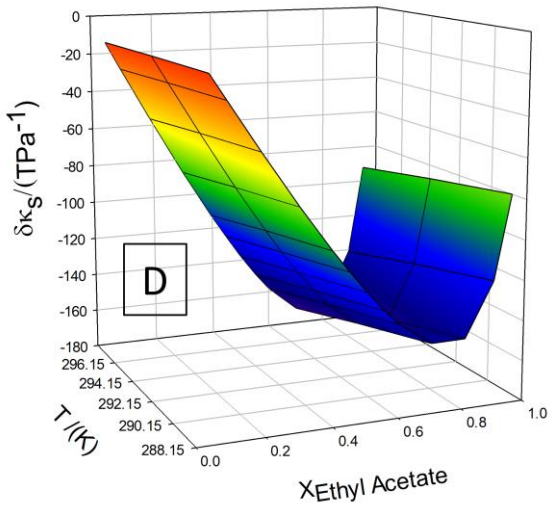


Figure 3. Surfaces of changes of refractive index on mixing of ((A) n-hexane and (B) ethyl acetate)) + olive oil mixtures at the range of temperatures 288.15–298.15 K and surfaces of changes of isentropic compressibilities of ((C) n-hexane and (D) ethyl acetate)) + olive oil mixtures at the range of temperatures 288.15-298.15 K

Table 6 Fitting parameters (eq. 3) and root mean square deviations (eq. 4) for changes of refractive indices on mixing (δn_D) and changes of isentropic compressibilities ($\delta\kappa_S$) with mole fraction for the studied mixtures as function of temperature.

Derived Property	B_{00}	B_{01}	B_{02}	B_{10}	B_{11}	B_{12}	B_{20}	B_{21}	B_{22}	B_{30}	B_{31}	B_{32}
						n-Hexane + Olive Oil						
δn_D	–1.569416E+00	1.142700E–02	–1.897338E–05	–7.741228E+00	5.344000E–02	–9.090107E–05	–4.612268E+00	3.204500E–02	–5.393833E–05	1.933739E+01	–1.318120E–01	2.261206E–04
						σ = 9.0E–04						
$\delta\kappa_S$ /(TPa^{-1})	-6.951074E+03	5.531864E+01	-1.223500E-01	-3.252600E+03	2.808745E+01	-6.944900E-02	6.546120E+03	-3.082865E+01	1.119100E-02	6.338051E+03	-2.679484E+01	2.004969E-04
						σ = 8.276						
						n-Heptane + Olive Oil						
δn_D	6.157432E+00	-4.178100E-02	7.189207E-05	-1.494935E+00	1.110900E-02	-1.930768E-05	-1.124295E+01	7.766400E-02	-1.330617E-04	6.157432E+00	-4.178100E-02	7.189207E-05
						σ = 5.9E-04						
$\delta\kappa_S$ /(TPa^{-1})	-1.411788E+04	1.006174E+02	-1.872210E-01	-4.509766E+04	3.149401E+02	-5.618400E-01	-6.874809E+04	4.758092E+02	-8.351560E-01	-1.411788E+04	1.006174E+02	-1.872210E-01
						σ = 6.210						
						n-Octane + Olive Oil						
δn_D	-2.813366E+00	1.953700E-02	-3.305685E-05	3.309499E+00	-2.221800E-02	3.817555E-05	2.347177E+00	-1.544900E-02	2.612376E-05	-2.813366E+00	1.953700E-02	-3.305685E-05
						σ = 4.0E-04						
$\delta\kappa_S$ /(TPa^{-1})	-6.807831E+02	7.702016E+00	-2.482400E-02	-8.727348E+03	6.608116E+01	-1.325320E-01	-7.089846E+04	4.895367E+02	-8.531710E-01	-6.807831E+02	7.702016E+00	-2.482400E-02
						σ = 3.989						
						n-Nonane + Olive Oil						
δn_D	-3.268780E-01	2.560954E-03	-4.224202E-06	-8.175710E-01	5.878134E-03	-9.838215E-06	-3.880076E+00	2.669700E-02	-4.537785E-05	-3.268780E-01	2.560954E-03	-4.224202E-06
						σ = 2.4E-04						
$\delta\kappa_S$ /(TPa^{-1})	1.030563E+04	-6.788977E+01	1.064190E-01	1.234711E+04	-8.053830E+01	1.247040E-01	-3.202516E+04	2.208822E+02	-3.864310E-01	1.030563E+04	-6.788977E+01	1.064190E-01
						σ = 2.628						
						Ethyl Acetate + Olive Oil						
δn_D	-2.745930E+00	1.932800E-02	-3.266165E-05	-7.086320E-01	5.398762E-03	-8.285304E-06	1.085279E+01	-7.313200E-02	1.250593E-04	-2.745930E+00	1.932800E-02	-3.266165E-05
						σ = 1.2E-03						
$\delta\kappa_S$ /(TPa^{-1})	3.009511E+03	-1.727985E+01	1.954300E-02	-8.247765E+03	6.233105E+01	-1.229430E-01	-9.837252E+03	7.412555E+01	-1.443380E-01	3.009511E+03	-1.727985E+01	1.954300E-02
						σ = 3.037						
						Vinyl Acetate + Olive Oil						
δn_D	-4.604430E-01	3.432079E-03	-5.318987E-06	-7.398330E-01	5.671864E-03	-9.232118E-06	1.856989E+00	-1.194900E-02	2.062344E-05	-4.604430E-01	3.432079E-03	-5.318987E-06
						σ = 9.4E-04						
$\delta\kappa_S$ /(TPa^{-1})	-8.312572E+02	8.940438E+00	-2.510900E-02	-3.152335E+03	2.843911E+01	-6.704700E-02	-3.568747E+03	3.238902E+01	-7.602100E-02	-8.312572E+02	8.940438E+00	-2.510900E-02
						σ = 5.631						
						Propyl Acetate + Olive Oil						
δn_D	-2.697414E+00	1.883500E-02	-3.175068E-05	9.196490E-01	-5.572343E-03	9.745868E-06	4.694506E+00	-3.111900E-02	5.289109E-05	-2.697414E+00	1.883500E-02	-3.175068E-05

						σ = 8.1E-04						
δκs /(TPa^{-1})	-1.178494E+04	8.316042E+01	-1.503910E-01	-2.979639E+04	2.085153E+02	-3.697840E-01	-4.454868E+04	3.097128E+02	-5.428890E-01	-1.178494E+04	8.316042E+01	-1.503910E-01
						σ = 2.489						
						Isopropyl Acetate + Olive Oil						
δn$_D$	2.189125E+00	-1.448800E-02	2.514124E-05	3.591805E+00	-2.387600E-02	4.120955E-05	-6.160423E+00	4.292900E-02	-7.328615E-05	2.189125E+00	-1.448800E-02	2.514124E-05
						σ = 8.9E-04						
δκs /(TPa^{-1})	-5.800561E+03	4.185520E+01	-7.867400E-02	-5.528279E+03	4.152651E+01	-8.178000E-02	7.910274E+03	-5.058529E+01	7.644500E-02	-5.800561E+03	4.185520E+01	-7.867400E-02
						σ = 1.963						
						Butyl Acetate + Olive Oil						
δn$_D$	7.170990E-01	-4.458244E-03	7.797277E-06	2.413420E+00	-1.588900E-02	2.723102E-05	-2.365500E-02	6.894787E-04	-1.092955E-06	7.170990E-01	-4.458244E-03	7.797277E-06
						σ = 5.7E-04						
δκs /(TPa^{-1})	-3.252600E+03	2.808745E+01	-6.944900E-02	6.546120E+03	-3.082865E+01	1.119100E-02	6.338051E+03	-2.679484E+01	2.004969E-04	-3.252600E+03	2.808745E+01	-6.944900E-02
						σ = 8.276						

Table 7. Root mean square deviations of experimental results from the estimated results for refractive indices on mixing by mixing rules (eqs. 5-13) at 298.15 K.

	L-L (*eq. 5*)	*G-D* (*eq. 6*)	*Ey* (*eq. 7*)	*A-B* (*eq. 8*)	*Nw* (*eq. 9*)	*Os* (*eq. 10*)	*E-J* (*eq. 11*)	*Wi* (*eq. 12*)	*He* (*eq. 13*)
	Additivity on Mixing								
n-Hexane	0.00403	0.00434	0.00425	0.00434	0.00467	0.00453	0.00419	0.01142	0.00338
n-Heptane	0.00184	0.00149	0.00160	0.00149	0.00116	0.00130	0.00166	0.00422	0.00207
n-Octane	0.00129	0.00101	0.00109	0.00101	0.00073	0.00085	0.00114	0.00323	0.00145
n-Nonane	0.00098	0.00075	0.00082	0.00075	0.00053	0.00062	0.00086	0.00252	0.00110
Ethyl Acetate	0.00028	0.00021	0.00011	0.00021	0.00063	0.00045	0.00011	0.00785	0.00102
Vinyl Acetate	0.00012	0.00033	0.00026	0.00033	0.00058	0.00047	0.00021	0.00467	0.00054
Propyl Acetate	0.00035	0.00009	0.00012	0.00009	0.00039	0.00024	0.00017	0.00579	0.00082
Isopropyl Acetate	0.00062	0.00022	0.00033	0.00022	0.00026	0.00013	0.00041	0.00666	0.00112
Butyl Acetate	0.00035	0.00008	0.00015	0.00008	0.00023	0.00011	0.00021	0.00438	0.00060
	Non Additivity on Mixing								
n-Hexane	0.00597	0.00608	0.00607	0.01092	0.00617	0.00619	0.01820	0.01167	0.00360
n-Heptane	0.00084	0.00073	0.00077	0.00396	0.00064	0.00070	0.00901	0.00433	0.00101
n-Octane	0.00067	0.00054	0.00058	0.00251	0.00045	0.00049	0.00568	0.00328	0.00137
n-Nonane	0.00057	0.00048	0.00052	0.00222	0.00042	0.00046	0.00492	0.00255	0.00104
Ethyl Acetate	0.00066	0.00026	0.00037	0.00098	0.00043	0.00027	0.00227	0.00779	0.00107
Vinyl Acetate	0.00049	0.00028	0.00033	0.00112	0.00035	0.00028	0.00257	0.00461	0.00058
Propyl Acetate	0.00057	0.00026	0.00034	0.00076	0.00032	0.00023	0.00161	0.00575	0.00085
Isopropyl Acetate	0.00063	0.00029	0.00038	0.00068	0.00035	0.00025	0.00134	0.00664	0.00113
Butyl Acetate	0.00044	0.00019	0.00026	0.00054	0.00024	0.00017	0.00109	0.00436	0.00067

Table 8. Root mean square deviations (eq. 4) of the experimental and estimated results for ultrasonic velocities ($m \cdot s^{-1}$) by different models (eqs. 14-19) at 298.15 K.

	Danusso (*eq. 14*)	*Nomoto* (*eq. 15*)	*Junjie* (*eq. 16*)	*Impedance Model* (*eq. 17*)	*CFT* (*eq. 18*)	*FLT* (*eq. 19*)
n-Hexane	47.53	5.36	42.25	87.01	86.51	91.66
n-Heptane	29.21	2.85	31.74	72.2	57.65	82.55
n-Octane	23.31	2.94	24.01	59.3	51.02	83.63
n-Nonane	25.33	3.09	18.71	49.69	41.97	81.06
Ethyl Acetate	23.03	11.59	0.81	90.02	60.82	96.28
Vinyl Acetate	17.33	12.01	2.50	100.66	70.32	92.23
Propyl Acetate	25.80	8.25	2.54	78.62	51.81	90.48
Isopropyl Acetate	6.75	8.32	8.82	95.05	77.78	95.86
Butyl Acetate	29.52	5.64	3.85	68.96	45.55	84.27

These mixtures show a high non-ideal trend which is severe conditioned by two phenomenon; the associative behaviour by dispersive forces among aliphatic ends and polar interactions among polar groups (ester functional groups) and the huge difference in molecular volume between each solvent and triglyceride (non polar flexible chains) that leads to important steric hyndrance effects. These factors, under mixing conditions, produce a) variation of the intermolecular forces and b) variation of molecular packing as a consequence of the size and shape differences between components, providing considerable non-ideality in this type of mixtures, and clearly two different trends. Firstly, solvents of aliphatic nature show contractive trend, inversely related to increasing chain size and directly related to rising temperatures (higher contraction for *n*-hexane that for *n*-nonane and stronger contraction for rising values of temperature), which is reflected as positive deviations in terms of change of refractive indices on mixing and strong negative deviations of change of isentropic compressibilities (Figures 1A and 2A). This tendency is coherent with earlier studies of this kind of mixtures [16] due to the easy packing of paraffinic chains into triglyceride molecules, in general terms.

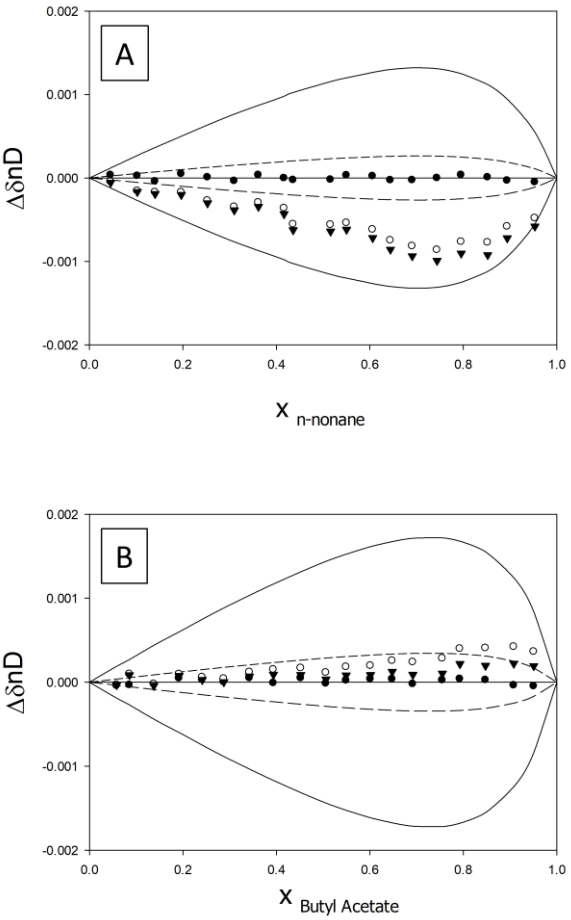


Fig. 4. Comparison of experimental and estimated data by Gladstone-Dale (●), Newton (○) and Oster (▼) for change of refractive index on mixing at 298.15 K, for ((a) n-nonane and (b) butyl acetate) + olive oil mixtures. The lines (----, 1% deviation; —, 5% deviation) indicate percentual deviation from experimental values as a reference.

As previously observed, pure paraffinic chains as n-alkane compounds are easily introduced among bulky hydrophobic side of glycerides mixing molecular volumes resulting in strong contractive trend mainly at the higher studied temperatures. These facts reveal as 1) higher temperature levels allow to access close empty spaces around macromolecules due to a higher molecular kinetics and 2) relative short paraffinic chains achieve more efficient disperse interaction without high level of steric hindrance (see comparison of n-nonane and n-hexane in terms of δn_D or excess molar volume [34]. Secondly, for mixtures containing esters and olive oil,

low temperatures deals for expansive trend, only isopropyl and butyl acetate mixtures showing contractive tendence at the highest temperatures. These trend are reflected too in terms of the studied properties change of refractive indices on mixing (positive values) and change of isentropic compressibilities (moderate negative values) (Figures 1B and 2B). For comparison, the evolution of n-hexane and ethyl acetate + olive oil are gathered as a funtion of composition and temperature in Figure 3 for both change of refractive index on mixing and change of isentropic compressibility.

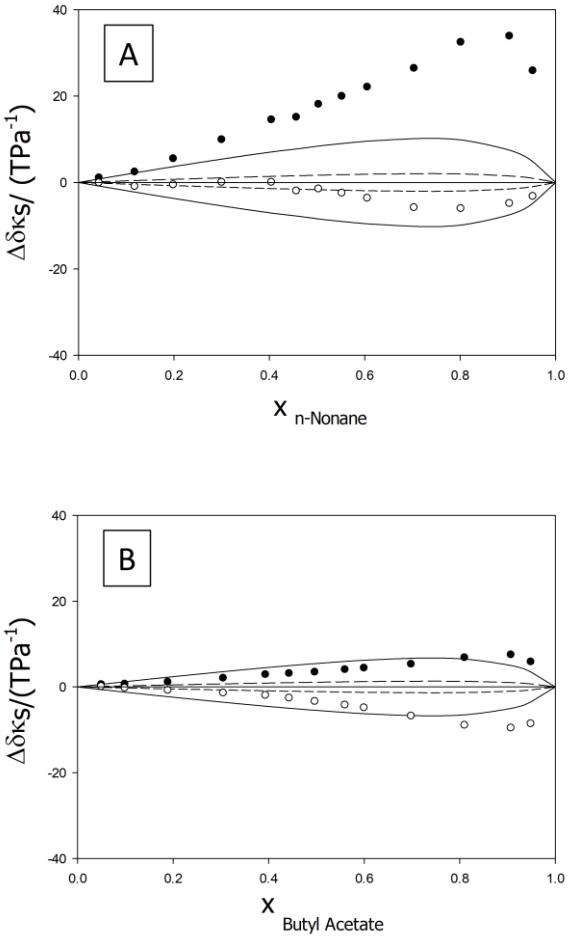


Fig.5. Comparison of experimental and estimated data by Junjie (●) and Nomoto (○) for change of isentropic compressibilities at 298.15 K, for ((a) n-nonane and (b) butyl acetate) + olive oil mixtures. The lines (----, 1% deviation; —, 5% deviation) indicate percentual deviation from experimental values as a reference.

As above commented upon, ester solvents introduce a relative polar charge around glicerides. Vinyl acetate is the most expansive case due to a combination of low molar mass and polar ester functional group – unsaturated group. This structure avoids an easy bulk packing among long chain triglycerides. On the other hand, isopropyl acetate gathers the highest contractive behavior into olive oil mixtures. This solvent shows an unique polar group besides a flat structure of apolar nature. As observed this solvent shows small negative values of change of isentropic compressibility, as corresponding with a potential low contractive solvent if compared with n-alkane tendency [16]. In what is referred to theoretical estimation, mixing rules for refractive index were applied [27], as well as different models for ultrasonic velocity [28-33] were applied. The best results in terms of estimation were gathered into Figures 4 and 5 for both derived properties, respectively. For the n-alkanes + olive oil mixtures, the Arago-Biot, Dale-Gladstone, Newton and Oster equations (eqs. 6, 8, 9, 10) show a better accuracy than the other studied procedures. For example, in Figure 4A and 4B experimental data of the authors for n-nonane + olive oil and butyl acetate + olive oil, respectively, are compared with the values estimated by the best methods. A good concordance are shown between our experimental data and those estimated, which gather a difference better than 1% for Gladstone-Dale equation and better than 5% for Newton and Oster equations for n-nonane mixtures. These methods gather better estimation capability for ester mixtures, all of them reaching deviations better than 1% (Figure 4B) when butyl acetate mixtures are analysed. For the estimation of ultrasonic velocities of the mixtures, two empirical models: Junjie and Nomoto were used for graphic presentation (Figures 5A-5B). These ultrasonic velocity estimation methods achieve results around 5% in deviation for n-nonane and butyl acetate. Only Junjie method shows greater deviations at higher hydrocarbon compositions as could be observed into Figure 5A. Attending to the obtained results, it could be concluded that the applied methods allow, at least, gathering a qualitative estimation of the mixing trend in terms of optical or acoustical properties at the studied range of temperatures for this kind of mixtures.

Acknowledgments
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Nomenclature
B_i – characteristic molecular volume (m^3)
B_{ij} – Fitting parameters of eq. 4
K – mathematical function of temperature
L_{mix} – intermolecular free length of a mixture (cm)
M_{eff} – effective molar mass of a mixture ($gmol^{-1}$)
M_i – molar mass of a pure compound ($gmol^{-1}$)
M_{oil} – molar mass of an oil ($gmol^{-1}$)
M_i – molar mass of each fatty acid according to the concentration analysis ($gmol^{-1}$)
$M_{CH-C-CH}$ – molar mass contributions of the triglyceride molecule axis fraction without three protons ($gmol^{-1}$)
M degree of the polynomial expansion (eq. 3)
NFA – number of fatty acid found by chromatographic analysis
n_D – refraction index of a mixture
n_{Di} – refraction index of a pure component
n_{DAT} – number of experimental data (eq. 4)
N – number of components into a mixture
P_{mix} – mixing thermodynamic magnitude
P_i – thermodynamic magnitude of a pure compound
R_i – molar sound velocity of a pure compound ($cm^3mol^{-1}(ms^{-1})^{1/3}$)
S degree of the polynomial expansion (eq. 3)
S – collision factor (eq. 18)

T – temperature (K)
u – ultrasonic velocity of a mixture (ms^{-1})
u_i – ultrasonic velocity of a pure compound (ms^{-1})
u_∞ - ultrasonic velocity constant (1600 ms^{-1})
V_i – molar volume of a pure compound (cm^3mol^{-1})
V_{mix} – molar volume of a mixture (cm^3mol^{-1})
x_i - molar fraction of i compound
x_j - molar fraction of j compound
Y_i – molar surface area of a pure compound (cm^2)
z – value of a property (eq. 4)
Z_i – specific acoustic impedance of a pure compound ($gcm^{-3}ms^{-1}$)
δP - change of a thermodynamic magnitude P for a mixture
δP_{ij} - change of a thermodynamic magnitude P for a mixture of i and j compounds
ϕ – volume fraction
ρ_{mix} - density of a mixture (gcm^{-3})
ρ_i - density of a pure component (gcm^{-3})
σ - root mean square deviation (eq. 4)

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