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Densities, Sound Velocities, and Refractive Indexes of Tetralin + *n*-Hexadecane at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K

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ABSTRACT: Mixtures of tetralin (1,2,3,4-tetrahydronaphthalene), an aromatic cyclic molecule, and *n*-hexadecane present asymmetries in chemical nature, shape, and chain length and are frequently found in kerosene and diesel fractions. Aiming at understanding the impact of these asymmetries on some thermophysical properties, this work presents densities, sound velocities, and refractive indexes for this binary system along with the properties of the pure components at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K over whole composition range and at atmospheric pressure. From these data, molar refractivity and excess volume were obtained. Several sound velocity mixing rules were tested, and the best result was for the Wada mixing rule. Pure component densities and sound velocities were correlated with the Prigogine−Flory−Patterson (PFP) model. The binary interaction parameter for this model was obtained from correlation of excess volumes. This model calculated experimental mixture densities very well and calculated reasonably good mixture sound velocities. A negative and high binary interaction parameter allowed us to describe positive excess volume.

INTRODUCTION

In many chemical engineering areas such as process design, oil fraction characterization, and others, accurate estimation of thermodynamic, optical, and ultrasonic properties as a function of composition and temperature is particularly important.[1] A considerable amount of work has been carried out on the measurement of these thermodynamic properties of liquid mixtures and the corresponding excess molar volumes.[2−4] In addition, many equations of state[5] have been developed to predict liquid mixture properties.

In this work, experimental density, ρ, sound velocity, u, and refractive index, n_D, data are reported at (293.15, 303.15, 313.15, 323.15, and 333.15) K for the binary system tetralin (1) + *n*-hexadecane (2).

In petroleum research, tetralin is a reference aromatic compound used to simulate kerosene and diesel fractions. In this sense, studies of densities, sound velocities, and refractive indexes of binary tetralin mixtures with *n*-hexadecane are intended to simulate kerosene or diesel fraction properties. These mixtures are asymmetrical in length, shape, and chemical nature, and then ideal solution behavior is not expected to work for these mixtures. For this reason, excess molar volumes, V^E, as a function of temperature and composition were analyzed. Density and sound velocity data were used to estimate the Prigogine−Flory−Patterson (PFP) model[6,7] parameters, allowing the correlation of pure component and mixture data and aiming at helping future studies involving tetralin mixtures.

Also, the previous excess volume results of Letcher and Scoones[8] and Chang et al.[9] remarkably differ in sign. Therefore, this work endeavors to present new data for this property, providing evidence for choosing the better data set.

EXPERIMENTAL SECTION

Tetralin (1,2,3,4-tetrahydronaphthalene) came from Reagen (Brazil), with purity more than 99.0 % in mass, obtained by gas chromatography. *n*-Hexadecane came from Vetec (Brazil), with purity more than 99.2 % in mass, also obtained by gas chromatography. No further purification was done.

Mixtures were prepared by transferring the pure liquids via pipet into stoppered bottles to prevent preferential evaporation, and the weight of the flask before and after addition of each substance was measured using a balance with a precision of $\pm 10^{-7}$ kg. The estimated uncertainty in the mole fractions was $\pm 1.3 \cdot 10^{-4}$. The flask was manually homogenized by shaking and then allowed to rest for some minutes before use. The density and sound velocity were obtained using an automatic digital densimeter (Anton Paar DSA 5000). The DSA 5000 simultaneously determines two physically independent properties within one sample. The instrument is equipped with a density cell and a sound velocity cell combining the known oscillating U-tube method with a highly accurate measurement of sound velocity.[10] The density and sound velocity meter was calibrated against triple-distilled fresh water and air at atmospheric pressure. The calibration was accepted if the measurements were estimated to be within $\pm (2 \cdot 10^{-3})$ kg·m^{-3} and ± 0.01 m·s^{-1} of the reference values. The refractive indexes at optical wavelength of 589.3 nm were obtained using an automatic digital refractometer (Rudolph J357). The refractometer was calibrated against triple-distilled fresh water and standard Canon oils.

In the calculation of averages for each state condition, each sample had at least two injections, and the outliers were discarded. A hydrocarbon more volatile than the pure components studied here was chosen as the worse scenario for determination of pure component standard uncertainty. More than ten different injections (different operators and days) were performed to measure density, sound velocity, and refractive

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index for *n*-decane at 313.15 K. The estimated standard uncertainties in density, sound velocity, and refractive index measurements are $(2 \cdot 10^{-2})$ $\text{kg} \cdot \text{m}^{-3}$, 0.1 $\text{m} \cdot \text{s}^{-1}$, and $4 \cdot 10^{-5}$, respectively. The uncertainty in the temperature is 0.01 K. Furthermore, these uncertainties were estimated also for mixtures according to the following procedure:

- The absolute difference between two measurements was calculated for all repetition data;
- The mixture uncertainty was considered the same for a given property independently of composition, temperature, or measurement order;
- Due to the previous consideration, all the absolute differences of a given property were considered samples of the same population;
- The mixture variance for a given property was calculated as half the variance in the absolute of differences obtained in two measurements performed at the same conditions;
- The pure tetralin and *n*-hexadecane data were not included in this calculation.

Following this procedure, the combined uncertainty in density, sound velocity, and refractive index measurements for mixtures was $5 \cdot 10^{-2}$ $\text{kg} \cdot \text{m}^{-3}$, 0.3 $\text{m} \cdot \text{s}^{-1}$, and $1 \cdot 10^{-4}$, respectively.

RESULTS AND DISCUSSION

Calculated Properties. From density (ρ), sound velocity (u), refractive index (n_D), and molecular weight (M) were obtained molar volume (V), molar refractivity (R_M), and excess molar volume (V^E), as presented in eqs 1, 2, and 3, respectively.

$$V = \frac{M}{\rho} \tag{1}$$

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} V \tag{2}$$

$$V^E = V - \sum_{i=1}^{2} x_i V_i \tag{3}$$

The mixture combined uncertainty in V is $1 \cdot 10^{-8}$ $\text{m}^3 \cdot \text{mol}^{-1}$, in V^E is $1.5 \cdot 10^{-8}$ $\text{m}^3 \cdot \text{mol}^{-1}$, and in R_M is $9 \cdot 10^{-9}$ $\text{m}^3 \cdot \text{mol}^{-1}$. The values of the excess volumes were fitted by the Redlich–Kister (RK) equation according to

$$V^E = x_1 x_2 [(A_0 + A_1 T^{-1} + A_2 T^{-2}) + (B_0 + B_1 T^{-1})(x_1 - x_2) + C_0 (x_1 - x_2)^2] \tag{4}$$

where T is the absolute temperature and A_0 to A_2; B_0, B_1; and C_0 are the fitting parameters. Excess volumes at all temperatures and mixture compositions (excluding pure components) were used in this procedure. The least-squares method was used to determine the values of the parameters.

Prigogine–Flory–Patterson Theory. In this paper, experimental density, sound velocity, and derived data have been correlated by the Prigogine–Flory–Patterson (PFP) model. Flory's model and other works that have resulted in the PFP model[6] are the most popular theoretical approaches to describe and/or predict some thermodynamic properties of many liquid multicomponent systems.[7] According to this model, an equation of state is applicable in reduced form to pure liquids and mixtures

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{(\tilde{V}^{1/3} - 1)} - \frac{1}{\tilde{V}\tilde{T}} \tag{5}$$

The reduced quantities are defined as

$$\tilde{p} = \frac{p}{p^*}, \ \tilde{T} = \frac{T}{T^*}, \text{ and } \tilde{V} = \frac{V}{V^*} \tag{6}$$

where p is the absolute pressure, and p^*, T^*, and V^* are characteristic parameters. For a binary mixture, we used the following mixing rules[7]

$$p^* = p_1^* \Phi_1 + p_2^* \Phi_2 + \frac{1}{2}(\Phi_1 \theta_2 + \Phi_2 \theta_1) X_{12} \tag{7}$$

$$T^* = \frac{p^*}{\left(\frac{p_1^*}{T_1^*}\right)\Phi_1 + \left(\frac{p_2^*}{T_2^*}\right)\Phi_2} \tag{8}$$

where X_{12} is an interaction parameter. For the determination of the properties of the mixture, some composition variables should be introduced: the segment fractions, Φ_1 and Φ_2, and the site fractions, θ_1 and θ_2, of the chemical species. They are defined as follows

$$\Phi_1 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*}, \ \Phi_2 = 1 - \Phi_1 \tag{9}$$

$$\theta_1 = \frac{s_1 \Phi_1}{s_1 \Phi_1 + s_2 \Phi_2}, \ \theta_2 = 1 - \theta_1 \tag{10}$$

where s_1 and s_2 are the molecular surface to volume ratios of both components, and the ratio between them is determined usually from the approximation of Abe and Flory[11]

$$\frac{s_1}{s_2} = \left(\frac{V_1^*}{V_2^*}\right)^{-1/3} \tag{11}$$

The weighted least-squares method has been used to fit the values of the characteristic parameters for pure components and binary mixture interaction parameters. The three PFP characteristic parameters for each substance were fitted to minimize the following objective function

$$F_{\text{obj}} = \sum_i \left(\frac{\rho_i^{\text{calcd}} - \rho_i^{\text{exp}}}{\delta\rho}\right)^2 + \left(\frac{u_i^{\text{calcd}} - u_i^{\text{exp}}}{\delta u}\right)^2 \tag{12}$$

where i indicates an experimental point; superscripts calcd and exp stand for calculated and experimental, respectively; and δ means the experimental uncertainty for pure substances. Data at all temperatures were used in this procedure, leading to a total of 12 data (six densities and six sound velocities) per pure substance. Initial guesses for these parameters were obtained elsewhere.[6,11]

The binary interaction parameter (X_{12}) was fitted to minimize the following objective function

$$F_{\text{obj}} = \sum_i \left(\frac{V_i^{\text{E, calcd}} - V_i^{\text{E, exp}}}{\delta V^E}\right)^2 \tag{13}$$

Here δ means the experimental uncertainty for mixtures. Excess volumes at all temperatures and mixture compositions (excluding pure components) were used in this procedure. Connection between equation of state properties and sound velocity is through eq 14. In this equation, C_p is the isobaric heat capacity, which is calculated considering the ideal solution theory and using pure component data from the literature.[12,13]

$$u = \left[\left(\frac{\partial \rho}{\partial p}\right)_T - \left(\frac{T}{\rho^2 C_p}\right)\left(\frac{\partial \rho}{\partial T}\right)_p^2\right]^{-1/2} \qquad (14)$$

Mixing Rules for Sound Velocity. Several mixing rules have being proposed to calculate mixture sound velocity from pure component data. In this work, the mixing rules of Rao,[14] eq 15, Nomoto,[15] eq 16, Wada,[16] eq 17, Van Dael,[17] eq 18, simplified ideal isentropic compressibility, eq 19, and collision factor theory,[18] eq 20, are studied. Also, we propose here a modification of the latter theory, based on the observation of the behavior of our data, and presented in eq 21, where the collision factor of the mixture was considered additive in volume fraction instead of in molar fraction. The expressions presented here were subject to proper rearrangement.

$$u^{1/3}V = \sum_{i=1}^{2} x_i u_i^{1/3} V_i \;\therefore\; u = \left(\frac{\sum_{i=1}^{2} x_i u_i^{1/3} V_i}{V}\right)^3 \qquad (15)$$

$$u = \left(\sum_{i=1}^{2} \phi_i u_i^{1/3}\right)^3 \qquad (16)$$

$$k_S^{-1/7} V = \sum_{i=1}^{2} x_i k_{S,i}^{-1/7} V_i \;\therefore\; u = \left(\frac{\sum_{i=1}^{2} x_i u_i^{2/7} \rho_i^{1/7} V_i}{\rho^{1/7} V}\right)^{7/2} \qquad (17)$$

$$\frac{1}{Mu^2} = \sum_{i=1}^{2} x_i \frac{1}{M_i u_i^2} \;\therefore\; u = \left(M \sum_{i=1}^{2} \frac{x_i}{M_i u_i^2}\right)^{-1/2} \qquad (18)$$

$$k_S = \sum_{i=1}^{2} \phi_i k_{S,i} \;\therefore\; u = \left(\rho \sum_{i=1}^{2} \phi_i k_{S,i}\right)^{-1/2} \qquad (19)$$

$$u = \frac{1}{V}\left(\sum_{i=1}^{2} x_i \frac{u_i V_i}{r_{S,i}^3}\right)\left(\sum_{i=1}^{2} x_i r_{S,i}^3\right) \qquad (20)$$

$$u = \frac{1}{V}\left(\sum_{i=1}^{2} \phi_i \frac{u_i V_i}{r_{S,i}^3}\right)\left(\sum_{i=1}^{2} x_i r_{S,i}^3\right) \qquad (21)$$

where ϕ_i is the volumetric fraction of component i; $k_S = 1/(u^2\rho)$ is the isentropic compressibility; and r_S is the molecular radius as calculated by Schaffs's collision factor theory.[18]

Discussion. A comparison between pure component properties obtained in this work and from the literature is presented in Table 1. As one can see, there is a very good agreement between our data and those presented elsewhere.

The experimental results and some derived properties are presented in Table 2. The greater packing of tetralin molecules leads to higher density. These smaller molecules present molar refractivity close to half of n-hexadecane. RK parameters of eq 4 are presented in Table 3.

Table 1. Comparison between Pure Component Density, ρ, Sound Velocity, u, and Refractive Index, n_D, at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K Obtained in This Work and from the Literature[a]

	$(10^{-3}\rho)/(\text{kg}\cdot\text{m}^{-3})$		$(u)/(\text{m}\cdot\text{s}^{-1})$		n_D	
T (K)	this work	literature	this work	literature	this work	literature
			n-Hexadecane			
293.15	0.77369	0.7733[19] 0.77338[20]	1357.1	1357.7[19] 1357[20]	1.43520	1.43453[21]
303.15	0.76675	0.7664[19] 0.76655[20]	1319.6	1320.2[19] 1319[20]	1.43106	1.43047[21]
313.15	0.75983	0.7594[19] 0.75968[20]	1283.4	1283.4[19] 1283[20]	1.42690	1.42650[22]
323.15	0.75291	0.7525[19] 0.75279[20]	1246.9	1247.4[19] 1246[20] 1248.11[23]	1.42279	-
333.15	0.74599	0.7456[19] 0.74586[20] 0.7462[9]	1211.6	1212.3[19] 1211[20]	1.41867	-
343.15	0.73907	0.7387[19] 0.73891[20]	1177.0	1177.9[19] 1176[20]	1.41448	-
			Tetralin			
293.15	0.96896	0.96893[24]	1488.6	1486.1[25]	1.54155	1.5415[26,27]
303.15	0.96102	0.96113[24] 0.95544[29]	1449.3	1447.8[28] 1477[29]	1.53687	1.5374[30]
313.15	0.95308	0.95323[24]	1410.7	-	1.53216	1.5330[30]
323.15	0.94513	0.9455[31,32] 0.9447[33]	1372.8	-	1.52752	-
333.15	0.93718	0.9387[34]	1336.4	-	1.52274	-
343.15	0.92922	-	1299.5	-	1.51795	-

[a] Standard uncertainties in density, sound velocity, and refractive index measurements are $2\cdot10^{-2}$ kg·m^{-3}, 0.1 m·s^{-1}, and $4\cdot10^{-5}$, respectively.

The correlation of densities and sound velocities with the PFP model led to average deviations from pure component properties of 0.01 kg·m^{-3} and −0.4 m·s^{-1}, which are within experimental expanded uncertainties, indicating the success of the parameter estimation. Minimum to maximum deviations are from (−1.6 to 1.4) kg·m^{-3} and (−11.6 to 13.7) m·s^{-1}, which are 2 orders of magnitude greater than the experimental uncertainties. It happens because the effect of temperature on the properties is misled, especially for sound velocity. The fitted values for the characteristic parameters and binary interaction parameter are summarized in Table 4. Dubey and Sharma[34] studied densities and sound velocities of n-hexadecane from (298.15 to 308.15) K and presented temperature-dependent PFP parameters, which are also presented in Table 4. The parameters obtained in this work are close to those of Dubey and Sharma,[34] with small differences in p^*. The X_{12} value found is significantly apart from zero, what indicates the significant nonideality in this mixture. Indeed, this parameter is negative, leading to a positive excess enthalpy, as expected for hydrocarbon mixtures.

Molar refractivity is intended to represent the molar volume actually occupied by molecules, which is supposed to be additive within the successful approximations of the Lorentz−Lorenz[35] mixing rule. Molar refractivity calculated by this mixing rule is

Table 2. Densities, ρ, Excess Molar Volume, V^E, Sound Velocities, u, Refractive Index, n_D, and Molar Refractivity, R_M, of the Binary Mixture Tetralin (1) + n-Hexadecane (2) at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K[a]

	$10^{-3}\rho$	10^6V^E	u		10^6R_M
x_1	$(kg \cdot m^{-3})$	$(m^3 \cdot mol^{-1})$	$(m \cdot s^{-1})$	n_D	$(m^3 \cdot mol^{-1})$
T/K = 293.15					
0.0000	0.77369	0.00	1357.1	1.4352	76.40
0.1004	0.78313	0.08	1361.4	1.4400	73.02
0.1987	0.79359	0.11	1366.5	1.4459	69.79
0.2934	0.80479	0.17	1371.3	1.4519	66.63
0.3996	0.81926	0.19	1379.2	1.4594	63.04
0.4981	0.83464	0.21	1387.8	1.4679	59.77
0.5989	0.85299	0.20	1399.2	1.4776	56.38
0.6991	0.87437	0.18	1412.9	1.4894	53.04
0.7993	0.89975	0.16	1431.2	1.5031	49.66
0.9003	0.93113	0.06	1455.7	1.5202	46.25
1.0000	0.96896	0.00	1488.6	1.5415	42.91
T/K = 303.15					
0.0000	0.76675	0.00	1319.6	1.4311	76.46
0.1004	0.77616	0.07	1324.1	1.4359	73.08
0.1987	0.78658	0.10	1329.3	1.4417	69.83
0.2934	0.79773	0.16	1334.0	1.4476	66.66
0.3996	0.81212	0.17	1342.0	1.4553	63.11
0.4981	0.82743	0.19	1350.7	1.4637	59.83
0.5989	0.84571	0.17	1362.0	1.4734	56.43
0.6991	0.86697	0.16	1375.5	1.4841	52.99
0.7993	0.89223	0.14	1393.3	1.4988	49.71
0.9003	0.92343	0.05	1417.7	1.5158	46.30
1.0000	0.96102	0.00	1449.3	1.5369	42.95
T/K = 313.15					
0.0000	0.75983	0.00	1283.4	1.4269	76.50
0.1004	0.76917	0.07	1287.4	1.4318	73.14
0.1987	0.77957	0.09	1292.7	1.4374	69.86
0.2934	0.79067	0.15	1297.4	1.4434	66.71
0.3996	0.80500	0.16	1305.4	1.4512	63.17
0.4981	0.82022	0.18	1314.1	1.4596	59.90
0.5989	0.83840	0.16	1325.3	1.4690	56.47
0.6991	0.85956	0.15	1338.7	1.4807	53.13
0.7993	0.88469	0.13	1356.1	1.4943	49.75
0.9003	0.91571	0.04	1379.6	1.5113	46.35
1.0000	0.95308	0.00	1410.7	1.5322	42.99
T/K = 323.15					
0.0000	0.75291	0.00	1246.9	1.4228	76.55
0.1004	0.76221	0.07	1251.4	1.4277	73.20
0.1987	0.77256	0.08	1256.8	1.4333	69.92
0.2934	0.78360	0.14	1261.5	1.4393	66.77
0.3996	0.79786	0.14	1269.4	1.4470	63.22
0.4981	0.81300	0.17	1278.1	1.4551	59.92
0.5989	0.83110	0.14	1289.2	1.4647	56.52
0.6991	0.85214	0.13	1302.4	1.4764	53.18
0.7993	0.87713	0.12	1319.4	1.4899	49.80
0.9003	0.90798	0.03	1342.6	1.5067	46.39
1.0000	0.94513	0.00	1372.8	1.5275	43.04
T/K = 333.15					
0.0000	0.74599	0.00	1211.6	1.4187	76.60
0.1004	0.75524	0.07	1216.1	1.4235	73.24
0.1987	0.76555	0.07	1221.5	1.4291	69.97
0.2934	0.77653	0.13	1226.2	1.4351	66.82
0.3996	0.79071	0.13	1234.1	1.4427	63.26
0.4981	0.80577	0.16	1242.7	1.4511	60.00
0.5989	0.82377	0.14	1253.6	1.4605	56.58
0.6991	0.84470	0.12	1266.7	1.4720	53.23
0.7993	0.86953	0.12	1283.2	1.4855	49.85
0.9003	0.90023	0.03	1306.3	1.5022	46.44
1.0000	0.93718	0.00	1336.4	1.5227	43.08
T/K = 343.15					
0.0000	0.73907	0.00	1177.0	1.4145	76.64
0.1004	0.74826	0.07	1181.3	1.4194	73.29
0.1987	0.75851	0.07	1186.9	1.4248	70.00
0.2934	0.76944	0.12	1191.5	1.4308	66.85
0.3996	0.78354	0.13	1199.0	1.4384	63.30
0.4981	0.79852	0.15	1207.7	1.4467	60.03
0.5989	0.81642	0.13	1218.5	1.4561	56.62
0.6991	0.83724	0.12	1231.4	1.4676	53.27
0.7993	0.86194	0.11	1248.3	1.4810	49.89
0.9003	0.89247	0.02	1270.7	1.4976	46.48
1.0000	0.92922	0.00	1299.5	1.5179	43.11

[a] Standard uncertainties in density, sound velocity, and refractive index measurements for mixtures were $5 \cdot 10^{-2}$ kg·m^{-3}, 0.3 m·s^{-1}, and $1 \cdot 10^{-4}$, respectively. The combined uncertainty in V^E is $1.5 \cdot 10^{-8}$ m^3·mol^{-1} and in R_M is $9 \cdot 10^{-9}$ m^3·mol^{-1}.

slightly higher than that obtained directly from our experimental values of refractive index and density. Deviations are from (2 to $5 \cdot 10^{-8}$) m^3·mol^{-1}, which is about the experimental combined uncertainty for this property.

Figure 1 shows experimental and PFP results for density and sound velocity data versus the mole fraction for the studied mixture. As one can see, the PFP model correlated well density and reasonably sound velocity, while their dependences with temperature have been misled, as already mentioned.

In Figure 2 are presented comparisons of excess volumes obtained in our work and elsewhere at (298.15 and 308.15) K[8] and at 333.15 K.[9] As one can see in Figure 2(a), the results of Chang et al.[9] are largely in disagreement with our data and with Letcher and Scoones's data.[8]

To provide an easier comparison between our data and those from Letcher and Scoones,[8] these two data sets are presented separately in Figure 2(b). One can find that there is a very good agreement between these data, although our excess volumes are slightly higher than those from the literature.

Figure 3 shows V^E at (293.15, 303.15, 333.15, and 343.15) K from experiments and calculated by RK (eqs 4) and by the PFP model over the whole composition range. Although not shown here, intermediate temperatures lead to intermediate excess properties. The error bar was plotted considering a 95 % confidence level (± 1.96 times the experimental standard

Table 3. Redlich−Kister Parameters for Excess Molar Volume, V^E

parameter	value
A_0	$(3.99 \cdot 10^{-6})$ m^3·mol^{-1}
A_1	$(-2.6 \cdot 10^{-3})$ m^3·mol^{-1}·K^{-1}
A_2	$(5.0 \cdot 10^{-1})$ m^3·mol^{-1}·K^{-2}
B_0	$(-4.3 \cdot 10^{-7})$ m^3·mol^{-1}
B_1	$(1.5 \cdot 10^{-4})$ m^3·mol^{-1}·K^{-1}
C_0	$(5.9 \cdot 10^{-8})$ m^3·mol^{-1}

Table 4. Fitted Values for the Prigogine−Flory−Patterson (PFP) Model Characteristic Parameters and Binary Interaction Parameters of Tetralin (1) + *n*-Hexadecane (2)

parameter	value from this work	values from literature[34]
P_1*	$(5.45 \cdot 10^2)$ MPa	-
T_1*	6233.8 K	-
V_1*	$(115.0 \cdot 10^{-6})$ m^3·mol^{-1}	-
P_2*	$(4.27 \cdot 10^2)$ MPa	(459.80, 452.14, and 459.95) MPa
T_2*	5874.4 K	(5600, 5613, and 5630) K
V_2*	$(243.4 \cdot 10^{-6})$ m^3·mol $^{-1}$	(240.1106, 240.2808, and 240.4950) m^3·mol^{-1}
X_{12}	−12.5 MPa	-

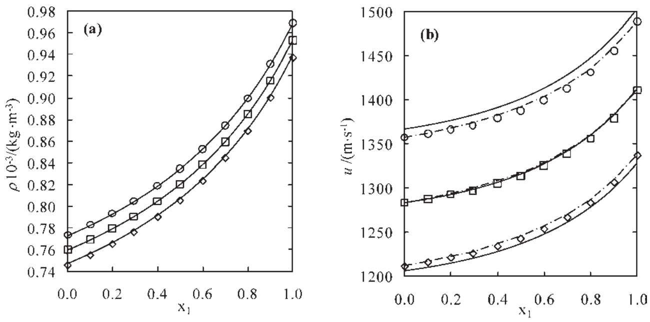

Figure 1. Effect of mixture composition upon densities (a), ρ/kg·m^{-3}, and sound velocities (b), u/m·s^{-1}, at ○, 293.15 K; □, 313.15 K; and ◇, 333.15 K. Solid lines have been calculated from the PFP model (eqs 5 to 11) using coefficients given in Table 4, and dot-dash lines are for the Wada mixing rule (eq 16).

uncertainty). As one can see, V^E are positive and nearly symmetrical. Following discussions presented by Kiyohara and Benson,[36] since there is a considerably high length and shape asymmetry between the pure substances, negative V^E was expected for this system. Thus, the obtained positive V^E indicates that an unfavorable cross intermolecular energy is the dominating effect in the studied conditions. This should be a consequence of an unfavorable packing between these asymmetrical molecules.

The PFP model correlates excess volumes misleading the temperature effect on this property. It is interesting to observe that the model calculates higher excess values at higher temperatures, which is the opposite of the experimental behavior.

The performances of sound velocity mixing rules are presented in Table 5. Interesting features may be identified in this

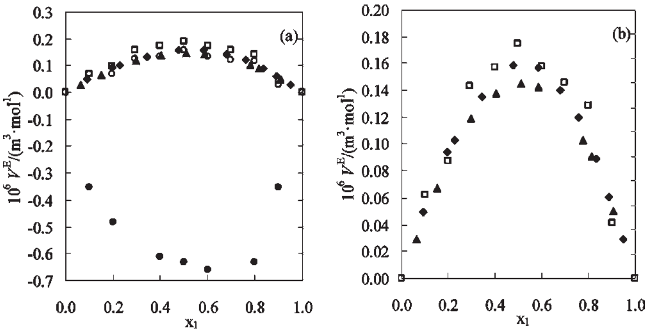

Figure 2. Excess volumes at □, 303.15 K; ♦, 298.15 K; ▲, 308.15 K; ●, 333.15 K; and ○, 333.15 K. (a) From this work and from two literature sources.[8,9] (b) From this work and from Letcher and Scoones.[8] Open symbols are for this work, and dark symbols are from the literature (♦ and ▲, Letcher and Scoones;[8] ●, Chang et al.[9]).

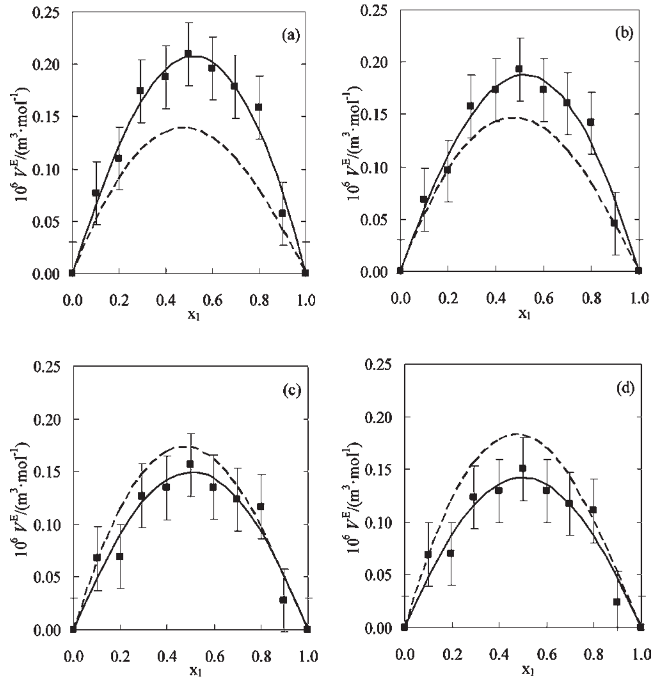

Figure 3. Excess volumes at (a) 293.15 K, (b) 303.15 K, (c) 333.15 K, and (d) 343.15 K. Solid lines stand for RK (eq 4) using coefficients given in Table 3, and dashed lines stand for PFP using coefficients given in Table 4.

evaluation. The difference in eqs 15 and 16 is that eq 15 employs an ideal solution volume fraction neglecting excess volume, while eq 16 does not. The difference in performance of these equations is 1 order of magnitude higher than the standard uncertainty in sound velocity. The best performance was for Wada, at all temperatures, that was also presented in Figure 1(b). Another interesting result is found comparing performances of eqs 20 and 21. The consideration that collision factor is additive in molar fraction led to a quite poor prediction of mixture sound velocity, while the modification proposed in this work considerably enhanced the model performance. Although not shown here, this conclusion is based not only on the results of Table 5 but also on the plot of collision factor versus molar fraction and volume fraction. Also not shown in the tables or graphics here, Rao[14] and

Table 5. Root-Mean-Square Deviation in Sound Velocity ($\mathrm{m \cdot s^{-1}}$), Excluding Pure Component Data, for the Studied Mixing Rules

T/K	eq 15	eq 16	eq 17	eq 18	eq 19	eq 20	eq 21
293.15	5.4	8.4	3.3	4.1	5.5	28.9	8.4
303.15	5.0	7.6	3.0	3.9	6.2	28.0	7.7
313.15	4.7	7.0	2.7	3.8	6.7	27.2	7.2
323.15	4.5	6.4	2.5	3.6	7.1	26.5	6.7
333.15	4.6	6.3	2.7	3.5	7.1	26.3	6.7
343.15	4.3	6.0	2.5	3.2	7.2	25.7	6.4
average	4.8	7.0	2.8	3.7	6.6	27.1	7.2

Wada[16] constants were calculated as functions of molar fraction, and very good linearity was found, as expected.

CONCLUSIONS

In this paper, we have experimentally determined density, sound velocity, and refractive index for the binary system tetralin + *n*-hexadecane. Data are reported at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K. To analyze the experimental results, we have calculated the excess molar volume over the temperature and composition intervals.

The system studied here presented positive excess volume, which were reasonably well correlated by the Prigogine—Flory—Patterson model. The model misled the temperature dependence of this property, although the overall performance was good.

The Wada constant was the best sound velocity mixing rule for the studied system. The collision factor in the collision factor theory was considered additive in volume fraction, and the results for sound velocity were considerably better than the original, molar fraction additive mixing rule.

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