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Densities of the binary systems n-hexane + n-decane and n-hexane + n-hexadecane up to 60 MPa and 463 K

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ABSTRACT

Density of the binary systems n-hexane + n-decane and n-hexane + n-hexadecane has been measured up to 60 MPa through a vibrating tube densimeter. Measurements covered the whole composition range, for the first system they were performed from (278.15 to 463.15)K, whereas for the latter from (298.15 to 463.15) K because n-hexadecane is solid at 278.15 K. Densities were correlated for every composition as a function of temperature and pressure through a modified Tammann-Tait equation with standard deviations lower than $8 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. Isothermal compressibility values were calculated from the experimental density data. Moreover, the excess volumes are reported, they were found to be negative for all the studied mixtures, with the absolute value lower or equal to $3.25 \text{ cm}^3 \cdot \text{mol}^{-1}$ for the system n-hexane + n-decane and $7.65 \text{ cm}^3 \cdot \text{mol}^{-1}$ for the system n-hexane + n-hexadecane. Various equations of state models were used to model the measured density data.

1. INTRODUCTION

Worldwide increase in oil consumption along with dwindling conventional oil and gas resources has led to progressive development of more challenging formations, which are deeper and characterized by more extreme temperature and pressure conditions. Oil exploitation under these conditions is risky and presents numerous technical difficulties, which leads to the need of new high pressure - high temperature technologies and equipment. Development of these new fields requires as well measurement and prediction of thermophysical data of reservoir fluids under extreme conditions, both for safe exploitation and for more accurate reservoir engineering calculation. However there is still a lack of data on these properties under high pressure and high temperature conditions, especially for mixtures. Due to the chemical complexity of reservoir fluids, it is a pragmatic method to represent them as a synthetic mixture of different hydrocarbons, which is easy to study and sometimes representative for a certain type of reservoir fluids. Moreover, in order to understand the interactions between pairs of compounds in reservoir fluids, it is preferable to study the behavior of the corresponding binary mixtures.

Density is one of the important thermophysical properties required for design and operation of the oil and gas production. It is used in calculation of oil reserves and serves as an indicator of the oil quality. It is employed in various reservoir engineering calculations, reservoir simulation, and

design of transport and processing facilities.^{1, 2} In this work we perform studies on density of two alkane binary mixtures from (278.15 to 463.15) K and up to 60 MPa in the whole composition range. Thus, we have studied the system n-hexane + n-decane, as well as a more asymmetric system n-hexane + n-hexadecane. To our knowledge two studies have been previously published on the high pressure density of the first system, firstly by Takagi and Teranishi³ who reported density of n-hexane + n-decane at 0.1, 50 and 100 MPa at 298.15 K in the whole composition range, and later by Quevedo-Nolasco et al.⁴ who reported data from (313.15 to 363.15)K up to 25 MPa, thus the density data reported in this work broadens the temperature and pressure range (except at 298.15 K) for the density of the system n-hexane + n-decane. As concerns the system n-hexane + n-hexadecane, experimental density data were previously reported by Dymond et al.⁵ from (298.15 to 373.15)K up to 500 MPa, hence the data presented in this work for this system broadens this temperature range both to lower and higher temperatures.

The density data reported in this work was correlated by means of a modified Tammann-Tait equation as a function of temperature and pressure for every binary mixture, whereas isothermal compressibility values were obtained by differentiation of the correlation. It was found that the compressibility is higher for the mixtures n-hexane + n-decane than for the mixtures n-hexane + n-hexadecane, when compared for the same pressure, temperature and mole fraction. Additionally, negative excess volumes are also found in the present work for both binary systems, being more negative for the system n-hexane + n-hexadecane than for the system n-hexane + n-decane.

The ability of several thermodynamic models to predict the density of the studied binary systems in the whole experimental temperature and pressure range was tested in this work. Thus, Soave-Redlich-Kwong (SRK)⁶, Peng-Robison (PR)⁷, PC-SAFT⁸ and Soave-Benedict-Webb-Rubin (S-BWR)⁹ EoSs were used to predict the experimental density data, finding the best prediction for the system n-hexane + n-decane through the S-BWR EoS (AAD%=0.3%) and for the system n-hexane + n-hexadecane through the PC-SAFT EoS (AAD%=0.6%).

2. MATERIALS AND METHODS

The chemicals used in this work, n-hexane, n-decane, n-dodecane and n-hexadecane were purchased from Sigma-Aldrich and the mole-fraction purity given by the manufacturer is presented in Table 1. These chemicals were used without further purification. Milli-Q water and n-dodecane were employed for densimeter calibration.

Table 1. Purity of materials

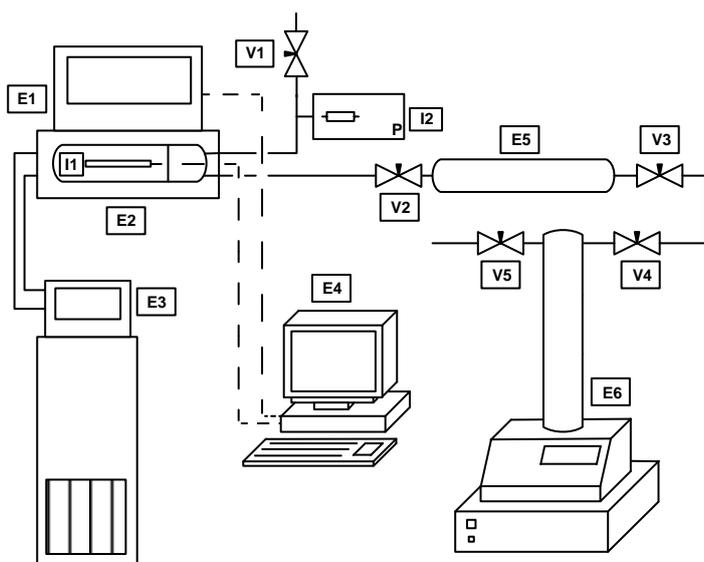
Chemical	CAS number	Mole-fraction purity*
n-hexane	110-54-3	0.992
n-decane	124-18-5	0.998
n-dodecane	112-40-3	0.998
n-hexadecane	544-76-3	0.994

*Gas chromatography (GC)

Binary mixtures were prepared gravimetrically by use of an analytical balance Mettler Toledo PR1203, which has a readability of $\pm 0.001\text{g}$. Five binary mixtures were prepared for the system n-hexane (1) + n-decane (2) with $x_1 = 0.1992, 0.3968, 0.4978, 0.5957$ and 0.7978 . As concerns the system n-hexane (1) + n-hexadecane (2), five mixtures were also prepared with $x_1 = 0.1985, 0.4136, 0.5007, 0.5966$ and 0.7928 . The expanded uncertainty of the mole fraction of the prepared mixtures was calculated according to the EA-4/02 M: 2013¹⁰, with a coverage factor $k = 2$, which corresponds to a coverage probability of 95%. It was found to be lower or equal to $1 \cdot 10^{-4}$ for the n-hexane + n-decane mixtures and lower or equal to $4 \cdot 10^{-4}$ for the n-hexane + n-hexadecane mixtures.

Figure 1 shows the scheme of the experimental setup. A vibrating tube densimeter Anton Paar DMA HPM measures the sample density through the frequency of vibration of an excited U-shaped tube. The oscillation periods are displayed with seven significant figures. Temperature regulation is performed through a circulating bath PolyScience PP07R-20-A12E which regulates temperature within $\pm 0.005\text{ K}$. Temperature is measured by means of a Pt100 probe located inside the measurement cell with an accuracy of $\pm 0.02\text{ K}$. Pressure is generated by means of a Teledyne Isco 100DX syringe pump, whereas it is measured through a digital pressure transducer SIKA type P that can perform pressure measurements up to 150 MPa with an accuracy of 0.05% FS (full scale). The syringe pump works with distillate water as hydraulic fluid and it is connected to an injection cylinder in which the sample is located; this injection cylinder contains a piston that separates the hydraulic fluid from the sample. When measuring density of n-hexadecane and their mixtures, the injection cylinder and the pipes were heated up to 323 K by means of heating bands in order to avoid solidification¹¹ of the studied sample.

Figure 1. Scheme of the experimental setup. (E1) mPDS 5 unit, (E2) DMA HPM measurement cell, (E3) thermostatic bath, (E4) computer, (E5) injection cylinder, (E6) syringe pump, (I1) Pt100, (I2) pressure transducer, (V1-V5) high pressure valves.



Temperature and period data are recorded through an Excel tool provided by Anton Paar. For every temperature and pressure condition, stability is considered to be achieved when the standard

deviation of the last thirty recorded values is lower than 0.02 K in temperature and $5 \cdot 10^{-3}$ μ s in oscillation period.

Densimeter was calibrated from (278.15 to 463.15)K up to 60 MPa following a procedure similar to that of Lagourette et al.¹² modified by Comuñas et al.¹³ using vacuum, Milli-Q water and n-dodecane as reference fluids. N-dodecane was employed as reference fluid under the temperature and pressure conditions where water is in vapor state, i.e. at $T \geq 373.15$ and $p = 0.1$ MPa and also at $T = 463.15$ K and $p = 1$ MPa.

Thus, for $T < 373.15$ K the equation employed to obtain the density values was:

$$\rho(T, p) = \rho_w(T, p) + \rho_w(T, 0.1 \text{ MPa}) \frac{\tau^2(T, p) - \tau_w^2(T, p)}{\tau_w^2(T, 0.1 \text{ MPa}) - \tau_v^2(T, 0)} \quad (1)$$

where ρ_w is the density of water reported by Wagner and Pruβ¹⁴ and τ , τ_w and τ_v are the oscillation periods for the measured sample, water and vacuum, respectively.

For $T \geq 373.15$ K and $p = 0.1$ MPa, as well as for $T = 463.15$ K and $p = 1$ MPa, the following equation was employed:

$$\rho(T, p) = \rho_d(T, p) + \rho_d(T, 0.1 \text{ MPa}) \frac{\tau^2(T, p) - \tau_d^2(T, p)}{\tau_d^2(T, 0.1 \text{ MPa}) - \tau_v^2(T, 0)} \quad (2)$$

where ρ_d is the density of n-dodecane reported by Lemmon and Huber¹⁵ and τ , τ_d and τ_v are the oscillation periods for the measured sample, n-dodecane and vacuum, respectively.

Finally, under any other conditions, i.e. $T = 373.15$ K and $T = 423.15$ K at $p > 0.1$ MPa, and $T = 363.15$ K at $p > 1$ MPa, the equation employed was:

$$\rho(T, p) = \rho_w(T, p) + \rho_d(T, 0.1 \text{ MPa}) \frac{\tau^2(T, p) - \tau_w^2(T, p)}{\tau_d^2(T, 0.1 \text{ MPa}) - \tau_v^2(T, 0)} \quad (3)$$

where τ , τ_w , τ_d and τ_v are the oscillation periods for the measured sample, water, n-dodecane and vacuum, respectively.

The expanded ($k=2$) uncertainty of the density measurements has been previously reported by Segovia et al.¹⁶ and it is considered to be $7 \cdot 10^{-4}$ $\text{g} \cdot \text{cm}^{-3}$ at $T < 373.15$ K, $5 \cdot 10^{-3}$ $\text{g} \cdot \text{cm}^{-3}$ at $T \geq 373.15$ K and $p = 0.1$ MPa, as well as for $T = 463.15$ K and $p = 1$ MPa, and $3 \cdot 10^{-3}$ $\text{g} \cdot \text{cm}^{-3}$ in other temperature and pressure conditions.

Density of n-hexane, n-decane and their binary mixtures was determined from (278.15 to 463.15) K up to 60 MPa. Regarding n-hexadecane and their binary mixtures with n-hexane, measurements were performed from (298.15 to 463.15) K up to 60 MPa or solidification pressure¹¹. The lowest pressure is determined by the vapor pressure of the pure n-hexane or the binary mixture.

3. MODELS

The prediction capability for density of the studied binary systems was evaluated for four different models, Soave-Redlich-Kwong EoS⁶ (SRK), Peng-Robinson EoS⁷ (PR), PC-SAFT EoS⁸ and Soave-Benedict-Webb-Rubin EoS⁹ (S-BWR).

3.1. Soave-Redlich-Kwong EoS⁶ (SRK)

The Soave-Redlich-Kwong EoS⁶ is given by:

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (4)$$

where R is the gas constant, V is the molar volume and a is the pure compound attractive parameter which has the following temperature dependency:

$$a(T) = a_c \left[1 + m(1 - \sqrt{T_r}) \right]^2 \quad (5)$$

where T_r is the reduced temperature (T/T_c , T_c being the critical temperature), a_c and m are given by the following expressions:

$$a_c = 0.42747 \frac{R^2 T_c^2}{p_c} \quad (6)$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \quad (7)$$

The pure compound co-volume parameter, b , is given by:

$$b = \frac{0.08664RT_c}{p_c} \quad (8)$$

where p_c is the critical pressure and ω is the acentric factor.

When dealing with mixtures, the attractive and co-volume parameters are calculated employing the conventional van der Waals one-fluid mixing rules.

3.2. Peng-Robinson EoS⁷ (PR)

The Peng-Robinson EoS⁷ is given by:

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (9)$$

where the pure compound attractive parameter $a(T)$ is obtained according to Eq. (5), being a_c , and m defined as follows:

$$a_c = 0.45724 \frac{R^2 T_c^2}{p_c} \quad (10)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (11)$$

The pure compound co-volume parameter, b , is given by:

$$b = \frac{0.07780RT_c}{p_c} \quad (12)$$

Conventional van der Waals one-fluid mixing rules were used.

3.3. PC-SAFT EoS⁸

The PC-SAFT EoS was developed by Gross and Sadowski⁸. The reduced residual Helmholtz free energy for mixtures containing non-associating fluids in PC-SAFT is given by:

$$a^r = a^{hs} + a^{chain} + a^{disp} \quad (13)$$

where a^{hs} and a^{chain} are the contributions from hard sphere segment-segment interaction and chain formation, respectively. The summation of these last two is the reference to build the dispersion force a^{disp} .

The simplified version of PC-SAFT proposed by von Solms et al.¹⁷, which reduces the computational time of this EoS, is used in this work.

Non-associating molecules are characterized by three pure-component parameters: the chain length m , the segment diameter σ and the segment energy ε . The van der Waals one-fluid mixing rules are applied to the dispersion term, whereas the conventional Berthelot-Lorentz combining rules are used for ε_{ij} and σ_{ij} .

3.4. Soave-Benedict-Webb-Rubin EoS⁹ (S-BWR)

The Soave modification⁹ of the Benedict-Webb-Rubin equation has the following form:

$$p = RT\rho\left(1 + B\rho + D\rho^4 + E\rho^2(1 + F\rho^2)\exp(-F\rho^2)\right) \quad (14)$$

Where ρ is the molar density and B , D , E and F are four model parameters. The value of these parameters at the critical point is obtained by the three critical constraints, $p_c = Z_c \rho_c RT_c$ and $(\partial p / \partial \rho)_{T_c} = (\partial^2 p / \partial \rho^2)_{T_c} = 0$, along with an empirical constraint $F = 0.77 / \rho_c^2$, where Z is the compressibility factor and the subscript c stands for the critical point. B , D , and E are treated as temperature dependent functions of the reduced temperature and acentric factor.

Soave developed the mixing rules by mixing T_c , p_c and ω in a way that the resulting mixing parameters in cubic EoS (a and b in SRK or PR) are as close as possible to their values calculated by the van der Waals mixing rules.

In total there are four parameters for each pure compound, i.e. T_c , p_c , ω and Z_c .

The values of the pure compound parameters employed in the EoSs analyzed in this work are gathered in Table 2.

Table 2. Pure compound parameters for SRK, PR, PC-SAFT and S-BWR EoSs.

	n-hexane	n-decane	n-hexadecane
T_c / K^*	507.60	617.70	723.00
p_c / MPa^*	3.025	2.110	1.400
$V_c / \text{cm}^3 \text{mol}^{-1}^*$	371	600	944
ω^*	0.3013	0.4923	0.7174
$\sigma / \text{\AA}^\S$	3.7983	3.8384	3.9552
$\epsilon k^{-1} / \text{K}^\S$	236.77	243.87	254.70
m^\S	3.0576	4.6627	6.6485

*DIPPR database¹⁸

[§]Gross and Sadowski⁸

4. RESULTS AND DISCUSSION

Densimeter calibration was verified by measuring density of n-dodecane in the whole temperature and pressure range, except for the temperature and pressure conditions where it was used for calibration, i.e. at $p = 0.1 \text{ MPa}$ and $T \geq 373.15 \text{ K}$ and also at $T = 463.15 \text{ K}$ and $p = 1 \text{ MPa}$. The measured density values for this compound are presented in Table 3.

Table 3. Density, ρ , of n-dodecane in $\text{g}\cdot\text{cm}^{-3}$.

p/MPa	T/K						
	278.15	298.15	323.15	348.15	373.15	423.15	463.15
0.10	0.7592	0.7456	0.7272	0.7087	–	–	–
1.00	0.7605	0.7462	0.7282	0.7096	0.6908	0.6526	–
5.00	0.7631	0.7490	0.7314	0.7134	0.6952	0.6587	0.6279
10.0	0.7662	0.7524	0.7353	0.7178	0.7004	0.6656	0.6369
20.0	0.7719	0.7587	0.7426	0.7261	0.7098	0.6776	0.6518
30.0	0.7773	0.7647	0.7492	0.7335	0.7181	0.6880	0.6642
40.0	0.7823	0.7701	0.7552	0.7402	0.7256	0.6970	0.6748
50.0	0.7871	0.7753	0.7609	0.7464	0.7325	0.7053	0.6841
60.0	0.7917	0.7802	0.7663	0.7523	0.7389	0.7128	0.6926

Expanded density uncertainty ($k=2$): $0.7 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at $T < 373.15 \text{ K}$; $5 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at $T \geq 373.15 \text{ K}$ and $p=0.1 \text{ MPa}$; $5 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at $T=463.15 \text{ K}$ and $p=1 \text{ MPa}$; $3 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at other temperature and pressure conditions. Temperature uncertainty: 0.02 K. Pressure uncertainty: 0.08 MPa.

In order to compare our experimental data with those from literature or with model predictions we have used in this work the Bias%, the absolute average deviation (AAD%), the maximum deviation ($D_{\max}\%$) as well as the standard deviation (σ). BIAS %, AAD% and σ are defined as follows:

$$\text{Bias \%} = \frac{100}{N} \sum_{i=1}^N \frac{Y_i^{\text{cal}} - Y_i^{\text{exp}}}{Y_i^{\text{exp}}} \quad (15)$$

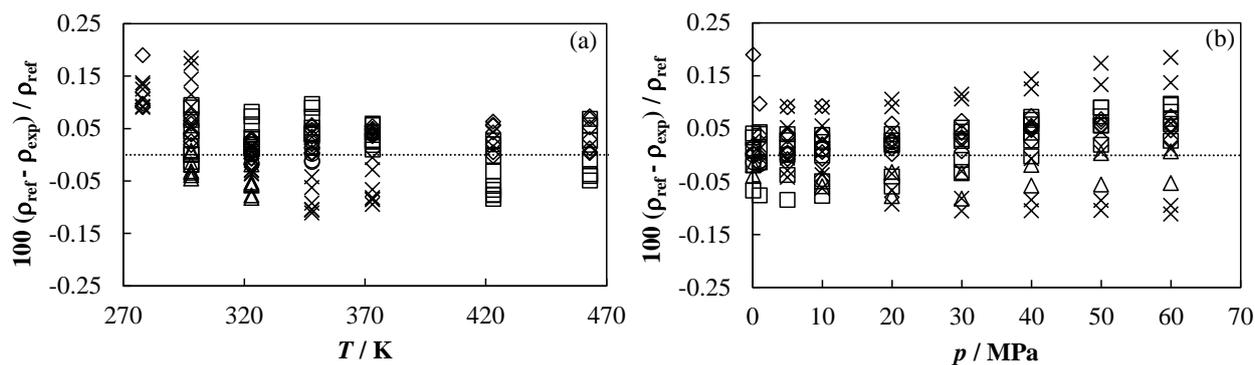
$$AAD\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{Y_i^{ref/cal} - Y_i^{exp}}{Y_i^{exp}} \right| \quad (16)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (Y_i^{exp} - Y_i^{cal})^2}{N - m}} \quad (17)$$

where Y_i^{exp} is the value of the experimental property determined in this work, $Y_i^{ref/cal}$ is the literature or the calculated value, N is the number of experimental data points and m is the number of parameters of the fit.

Density values obtained for n-dodecane were compared with data interpolated through the Tait-type correlation reported by Caudwell et al.¹⁹ from (298.15 to 463.15)K up to 60 MPa yielding an AAD% of 0.04%. Valencia et al.²⁰ reported also density data for n-dodecane from (283.15 to 323.15) K up to 60 MPa, thus we have compared the values obtained in this work with those from Valencia et al.²⁰ at 298.15 K and 323.15 K in the whole pressure range yielding an AAD% of 0.04%. Moreover, Elizalde-Solís et al.²¹ have also reported density data of n-dodecane from (213.09 to 362.29) K up to 25 MPa, we have compared the density values reported in the present work with those obtained from the correlation given by Elizalde-Solís et al.²¹ at 323.15 K and 348.15 K up to 20 MPa obtaining an AAD% of 0.01%. Additionally, the AAD% among our experimental data and the data obtained through the EoS given by Lemmon and Huber¹⁵ in the whole experimental temperature and pressure range is 0.04%. Finally, the density data obtained for n-dodecane in this work were also compared with data obtained from the correlation published by Cibulka and Hnědkovský²² taking into account the temperature and pressure limits given for the correlation, so the range for comparison was limited to temperatures lower than 393.15 K and pressures higher than 2.03 MPa, the obtained AAD% was 0.08%. The overall AAD%, taking into account all the aforementioned literature data, was 0.05%, which is within the combined uncertainty of the considered experimental techniques. A deviation plot for n-dodecane density is presented in Figure 2.

Figure 2. Relative deviations between the n-dodecane density data measured in this work and those from literature (a) against temperature and (b) against pressure. (\diamond) Lemmon and Huber¹⁵, (\square) Caudwell et al.¹⁹, (\triangle) Valencia et al.²⁰, (\times) Cibulka and Hnědkovský²², (\circ) Elizalde-Solís et al.²¹.



The density of n-hexane, n-decane and n-hexadecane measured in this work is gathered in Table 4.

Table 4. Density, ρ , of n-hexane, n-decane and n-hexadecane in $\text{g}\cdot\text{cm}^{-3}$.

p/MPa	T/K						
	278.15	298.15	323.15	348.15	373.15	423.15	463.15
n-hexane							
0.10	0.6733	0.6561	0.6317	–	–	–	–
1.00	0.6739	0.6559	0.6331	0.6085	0.5826	0.5212	–
5.00	0.6776	0.6601	0.6382	0.6149	0.5910	0.5369	0.4842
10.0	0.6818	0.6651	0.6442	0.6221	0.6000	0.5515	0.5085
20.0	0.6896	0.6739	0.6547	0.6346	0.6148	0.5732	0.5389
30.0	0.6968	0.6819	0.6639	0.6452	0.6270	0.5897	0.5598
40.0	0.7032	0.6890	0.6719	0.6544	0.6374	0.6032	0.5759
50.0	0.7092	0.6955	0.6793	0.6626	0.6466	0.6146	0.5893
60.0	0.7150	0.7017	0.6861	0.6702	0.6549	0.6248	0.6007
n-decane							
0.10	0.7416	0.7267	0.7074	0.6876	0.6671	0.6248	–
1.00	0.7422	0.7274	0.7084	0.6886	0.6688	0.6272	0.5904
5.00	0.7450	0.7305	0.7119	0.6928	0.6738	0.6345	0.6003
10.0	0.7483	0.7342	0.7162	0.6977	0.6796	0.6424	0.6108
20.0	0.7544	0.7409	0.7240	0.7067	0.6898	0.6558	0.6278
30.0	0.7601	0.7472	0.7311	0.7146	0.6988	0.6671	0.6414
40.0	0.7654	0.7530	0.7375	0.7218	0.7068	0.6770	0.6531
50.0	0.7704	0.7584	0.7435	0.7284	0.7141	0.6859	0.6633
60.0	0.7753	0.7637	0.7492	0.7346	0.7208	0.6938	0.6721
n-hexadecane							
0.10	–	0.7705	0.7531	0.7356	0.7178	0.6808	0.6516
1.00	–	0.7711	0.7539	0.7365	0.7194	0.6841	0.6545
5.00	–	0.7736	0.7568	0.7398	0.7232	0.6892	0.6610
10.0	–	0.7769	0.7604	0.7438	0.7277	0.6951	0.6685
20.0	–	0.7826	0.7669	0.7511	0.7359	0.7055	0.6812
30.0	–	0.7881	0.7729	0.7578	0.7434	0.7147	0.6920
40.0	–	–	0.7785	0.7639	0.7503	0.7229	0.7014
50.0	–	–	0.7838	0.7697	0.7565	0.7304	0.7098
60.0	–	–	0.7887	0.7751	0.7624	0.7372	0.7175

Expanded density uncertainty ($k=2$): $0.7\cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at $T < 373.15 \text{ K}$; $5\cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at $T \geq 373.15 \text{ K}$ and $p=0.1 \text{ MPa}$; $5\cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at $T=463.15 \text{ K}$ and $p=1 \text{ MPa}$; $3\cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$ at other temperature and pressure conditions. Temperature uncertainty: 0.02 K. Pressure uncertainty: 0.08 MPa.

Density data of the compounds presented in Table 4, as well as those of n-dodecane, were correlated as a function of temperature and pressure by using a modified Tammann-Tait equation that has the following form:

$$\rho(T, p) = \frac{\rho(T, 0.1 \text{MPa})}{1 - C \cdot \ln\left(\frac{B(T) + p}{B(T) + 0.1 \text{MPa}}\right)} \quad (18)$$

where $\rho(T, 0.1 \text{MPa})$ is the density as a function of temperature at atmospheric pressure, given by the following polynomial equation:

$$\rho(T, 0.1 \text{MPa}) = \sum_{i=0}^m A_i T^i \quad (19)$$

C is a parameter independent of temperature and pressure and $B(T)$ is a temperature dependent parameter given by the following polynomial equation:

$$B(T) = \sum_{j=0}^n B_j T^j \quad (20)$$

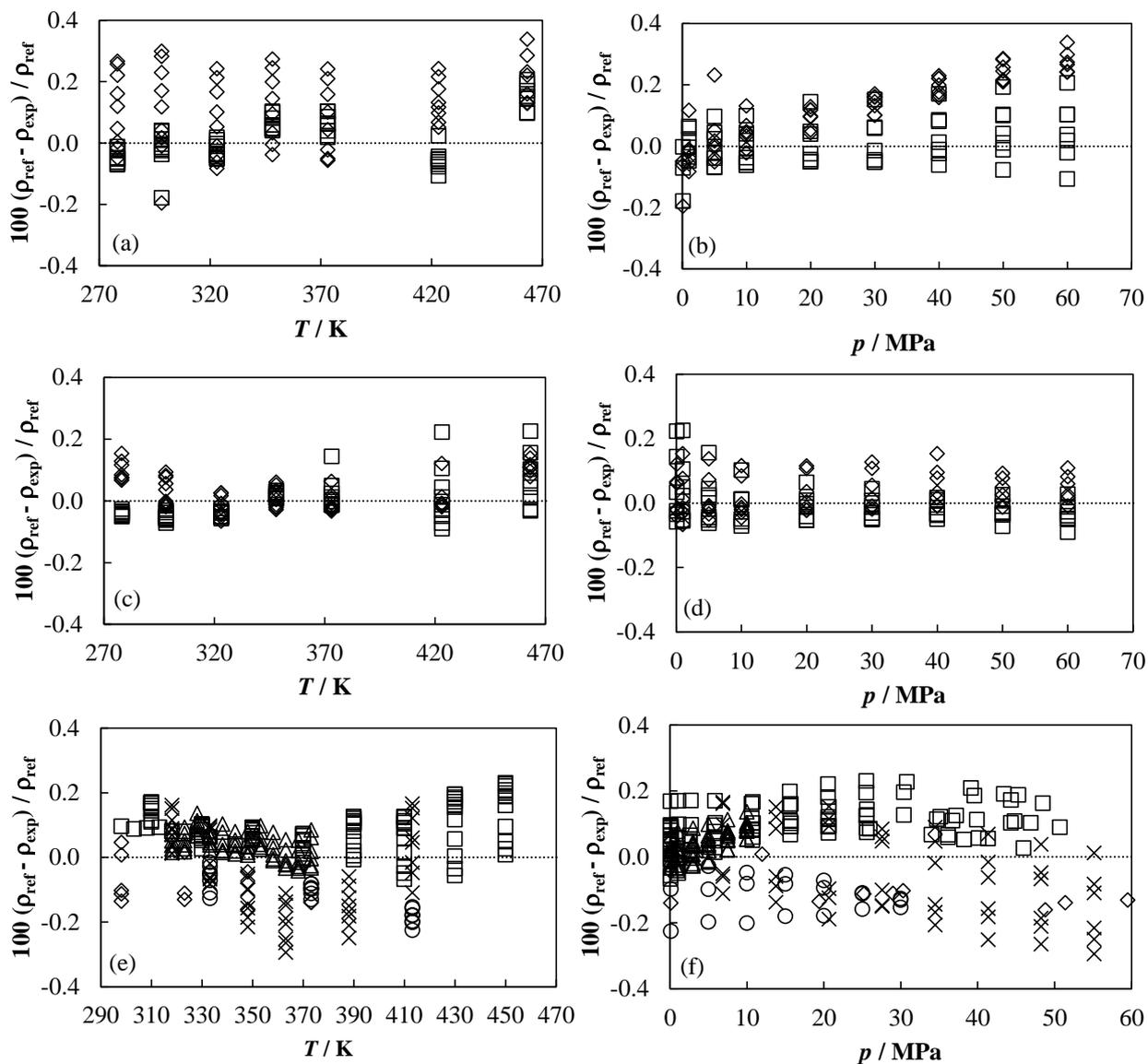
Parameters of this fit are presented in Table 5 for the pure compounds studied in this work, i.e. n-hexane, n-decane, n-dodecane and n-hexadecane. It must be noted that for n-hexane at temperatures higher or equal to 348.15 K and for n-decane at 463.15 K, the saturated densities^{23, 24} were employed for obtaining the fitting parameters of Eq. (18). Standard deviations for these fits are lower than $8 \cdot 10^{-4} \text{g} \cdot \text{cm}^{-3}$.

Table 5. Fitting parameters of the modified Tammann-Tait equation (Eq. 18), standard deviation of the fit (σ), $D_{\max}\%$, BIAS% and AAD% for n-hexane, n-decane, n-dodecane and n-hexadecane.

	n-hexane	n-decane	n-dodecane	n-hexadecane
$A_0/\text{g} \cdot \text{cm}^{-3}$	1.2299	0.9627	0.9516	0.9988
$10^4 \cdot A_1/\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$	-39.72	-9.445	-7.074	-9.101
$10^7 \cdot A_2/\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-2}$	103.2	9.063	1.995	7.278
$10^9 \cdot A_3/\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$	-11.63	-1.325	-0.49	-0.8163
C	0.08765	0.08537	0.08616	0.07881
B_0/MPa	309.4	339.9	351.5	348.9
$B_1/\text{MPa} \cdot \text{K}^{-1}$	-1.219	-1.205	-1.201	-1.174
$10^4 \cdot B_2/\text{MPa} \cdot \text{K}^{-2}$	12.05	11.01	10.67	10.37
$10^4 \cdot \sigma/\text{g} \cdot \text{cm}^{-3}$	7.7	2.0	1.7	3.3
$D_{\max}\%$	0.49	0.09	0.07	0.20
Bias%	0.00	-0.01	-0.01	0.01
AAD%	0.08	0.02	0.02	0.03

Density results obtained for n-hexane, n-decane and n-hexadecane were also compared with literature values. Thus, for n-hexane our experimental data were compared with data from the correlation published by Span and Wagner²⁴ obtaining an AAD% of 0.14 % and also with data from the correlation of Cibulka and Hnědkovský²² yielding an AAD% of 0.06%. Concerning density data of n-decane, our experimental data were compared with those obtained from the correlation reported by Lemmon and Span²³ finding an AAD% of 0.04% and with the correlation by Cibulka and Hnědkovský²² obtaining an AAD% of 0.05%. Finally, our correlated density data of n-hexadecane were compared with data reported by Dymond et al.⁵ up to 373.15 K and 60 MPa yielding an AAD% of 0.10%, with data published by Outcalt et al.²⁵ up to 50 MPa finding an AAD% of 0.10%, with data published by Amorin et al.²⁶ up to 413.15 K and 60 MPa obtaining an AAD% of 0.12 %, with data reported by Banipal et al.²⁷ up to 373.15 K and 10 MPa yielding an AAD of 0.05% and with data from Chang et al.²⁸ up to 413.15 K and 30 MPa with an AAD% of 0.12%. Deviation plots for these last fluids can be observed in Figure 3.

Figure 3. Relative deviations between n-hexane, n-decane and n-hexadecane density data measured in this work and those from literature as a function of temperature and pressure. (a,b) n-hexane: (\diamond) Span and Wagner²⁴, (\square) Cibulka and Hnědkovský²²; (c,d) n-decane: (\diamond) Lemmon and Span²³, (\square) Cibulka and Hnědkovský²²; (e,f) n-hexadecane: (\diamond) Dymond et al.⁵, (\square) Outcalt et al.²⁵, (\triangle) Banipal et al.²⁷, (\circ) Chang et al.²⁸, (\times) Amorin et al.²⁶.



As concern the binary mixtures, density values of the system n-hexane + n-decane are presented in Table 6, whereas those of the system n-hexane + n-hexadecane are presented in Table 7. As expected, for the same composition density of the mixtures n-hexane + n-hexadecane is higher than that of the mixtures n-hexane + n-decane (Figure 4), as density increases with the carbon number of n-alkanes due to decrease on the intermolecular free space.

Table 6. Densities, ρ , of the binary mixture n-hexane (1) + n-decane (2) in $\text{g}\cdot\text{cm}^{-3}$

p/MPa	T/K						
	278.15	298.15	323.15	348.15	373.15	423.15	463.15
	$x_1 = 0.1992$						
0.1	0.7324	0.7168	0.6975	0.6770	–	–	–
1.0	0.7330	0.7175	0.6986	0.6781	0.6577	0.6144	–
5.0	0.7358	0.7207	0.7023	0.6825	0.6630	0.6222	0.5863
10.0	0.7392	0.7246	0.7067	0.6877	0.6690	0.6306	0.5978

20.0	0.7456	0.7317	0.7148	0.6971	0.6799	0.6449	0.6161
30.0	0.7515	0.7381	0.7221	0.7053	0.6893	0.6568	0.6307
40.0	0.7569	0.7440	0.7286	0.7127	0.6976	0.6671	0.6429
50.0	0.7619	0.7496	0.7349	0.7195	0.7050	0.6762	0.6534
60.0	0.7670	0.7550	0.7407	0.7258	0.7118	0.6844	0.6627
$x_1=0.3968$							
0.1	0.7214	0.7056	0.6854	–	–	–	–
1.0	0.7221	0.7063	0.6865	0.6657	0.6450	0.5991	–
5.0	0.7251	0.7097	0.6905	0.6704	0.6507	0.6078	0.5702
10.0	0.7287	0.7138	0.6953	0.6760	0.6571	0.6171	0.5833
20.0	0.7351	0.7210	0.7037	0.6858	0.6685	0.6325	0.6033
30.0	0.7414	0.7279	0.7113	0.6944	0.6783	0.6453	0.6188
40.0	0.7470	0.7342	0.7182	0.7022	0.6870	0.6562	0.6317
50.0	0.7522	0.7399	0.7246	0.7093	0.6948	0.6657	0.6428
60.0	0.7574	0.7454	0.7306	0.7159	0.7019	0.6743	0.6527
$x_1=0.4978$							
0.1	0.7154	0.6991	0.6782	–	–	–	–
1.0	0.7160	0.6996	0.6794	0.6582	0.6367	0.5894	–
5.0	0.7192	0.7031	0.6836	0.6632	0.6426	0.5988	0.5595
10.0	0.7228	0.7073	0.6883	0.6688	0.6494	0.6086	0.5735
20.0	0.7295	0.7148	0.6971	0.6790	0.6613	0.6248	0.5946
30.0	0.7357	0.7217	0.7049	0.6878	0.6714	0.6379	0.6107
40.0	0.7414	0.7280	0.7119	0.6957	0.6802	0.6490	0.6241
50.0	0.7468	0.7338	0.7185	0.7030	0.6882	0.6588	0.6355
60.0	0.7520	0.7394	0.7246	0.7097	0.6955	0.6675	0.6456
$x_1=0.5957$							
0.1	0.7085	0.6921	0.6709	–	–	–	–
1.0	0.7091	0.6927	0.6721	0.6503	0.6281	0.5789	–
5.0	0.7123	0.6962	0.6763	0.6555	0.6344	0.5889	0.5479
10.0	0.7160	0.7005	0.6813	0.6614	0.6414	0.5992	0.5631
20.0	0.7228	0.7082	0.6903	0.6719	0.6537	0.6162	0.5854
30.0	0.7293	0.7152	0.6983	0.6810	0.6641	0.6298	0.6023
40.0	0.7351	0.7216	0.7055	0.6891	0.6732	0.6413	0.6160
50.0	0.7406	0.7276	0.7121	0.6964	0.6813	0.6513	0.6276
60.0	0.7458	0.7333	0.7184	0.7032	0.6888	0.6602	0.6379
$x_1=0.7978$							
0.1	0.6926	0.6755	0.6534	–	–	–	–
1.0	0.6933	0.6763	0.6546	0.6319	0.6084	0.5546	–
5.0	0.6968	0.6803	0.6593	0.6375	0.6154	0.5665	0.5211
10.0	0.7006	0.6848	0.6647	0.6440	0.6232	0.5787	0.5394
20.0	0.7079	0.6930	0.6743	0.6553	0.6366	0.5975	0.5651
30.0	0.7147	0.7004	0.6828	0.6650	0.6478	0.6124	0.5838
40.0	0.7208	0.7072	0.6904	0.6736	0.6575	0.6248	0.5985
50.0	0.7264	0.7134	0.6974	0.6814	0.6662	0.6357	0.6110
60.0	0.7319	0.7193	0.7039	0.6885	0.6740	0.6453	0.6218

Expanded density uncertainty ($k=2$): $0.7 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T < 373.15 \text{ K}$; $5 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T \geq 373.15 \text{ K}$ and $p=0.1 \text{ MPa}$; $5 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T=463.15 \text{ K}$ and $p=1 \text{ MPa}$; $3 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at other temperature and pressure conditions. Expanded mole fraction uncertainty ($k=2$): $1 \cdot 10^{-4}$. Temperature uncertainty: 0.02 K . Pressure uncertainty: 0.08 MPa .

Table 7

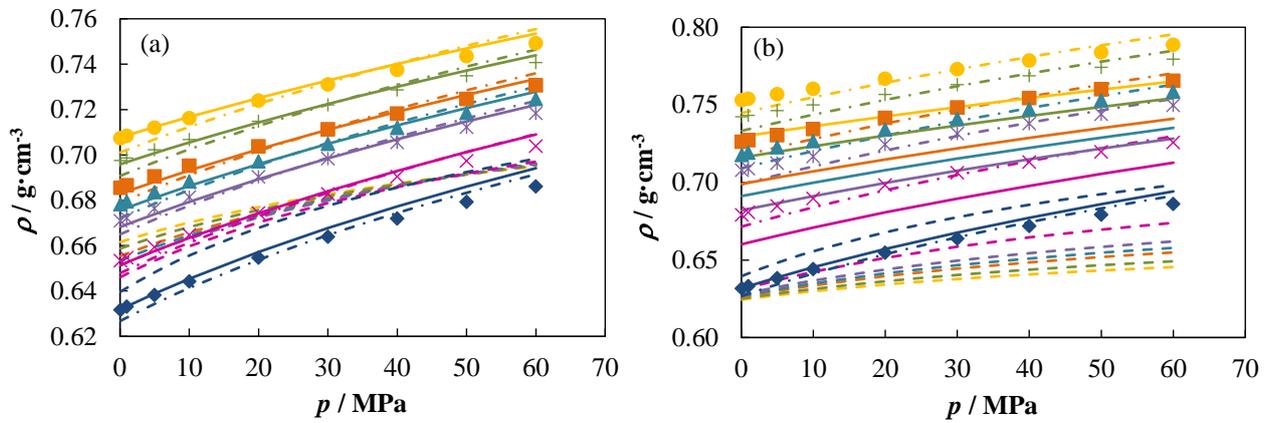
Densities, ρ , of the binary mixture n-hexane (1) + n-hexadecane (2) in $\text{g}\cdot\text{cm}^{-3}$

p/MPa	T/K					
	298.15	323.15	348.15	373.15	423.15	463.15
$x_1 = 0.1985$						
0.1	0.7597	0.7423	0.7244	0.7066	0.6688	–
1.0	0.7603	0.7432	0.7252	0.7075	0.6708	0.6403
5.0	0.7630	0.7462	0.7287	0.7117	0.6763	0.6475
10.0	0.7663	0.7499	0.7329	0.7164	0.6825	0.6555
20.0	0.7723	0.7567	0.7406	0.7252	0.6937	0.6691
30.0	0.7779	0.7630	0.7476	0.7330	0.7033	0.6806
40.0	0.7832	0.7687	0.7540	0.7401	0.7119	0.6905
50.0	0.7881	0.7742	0.7600	0.7466	0.7197	0.6993
60.0	–	0.7794	0.7656	0.7527	0.7268	0.7074
$x_1 = 0.4136$						
0.1	0.7444	0.7262	0.7080	0.6891	–	–
1.0	0.7451	0.7271	0.7090	0.6902	0.6513	0.6182
5.0	0.7480	0.7304	0.7128	0.6948	0.6576	0.6265
10.0	0.7514	0.7344	0.7173	0.6999	0.6645	0.6356
20.0	0.7578	0.7416	0.7256	0.7094	0.6766	0.6507
30.0	0.7637	0.7483	0.7330	0.7177	0.6871	0.6632
40.0	0.7692	0.7543	0.7397	0.7253	0.6963	0.6739
50.0	0.7744	0.7601	0.7460	0.7323	0.7046	0.6834
60.0	0.7795	0.7654	0.7519	0.7387	0.7121	0.6920
$x_1 = 0.5007$						
0.1	0.7367	0.7177	0.6983	–	–	–
1.0	0.7375	0.7191	0.7001	0.6810	0.6409	0.6061
5.0	0.7404	0.7226	0.7040	0.6858	0.6476	0.6152
10.0	0.7440	0.7267	0.7086	0.6912	0.6549	0.6249
20.0	0.7504	0.7341	0.7172	0.7010	0.6676	0.6409
30.0	0.7565	0.7410	0.7249	0.7097	0.6785	0.6540
40.0	0.7622	0.7472	0.7318	0.7175	0.6880	0.6651
50.0	0.7675	0.7530	0.7382	0.7246	0.6965	0.6749
60.0	0.7726	0.7585	0.7442	0.7312	0.7042	0.6836
$x_1 = 0.5966$						
0.1	0.7269	0.7078	0.6872	–	–	–
1.0	0.7275	0.7089	0.6893	0.6699	0.6282	0.5930
5.0	0.7306	0.7124	0.6935	0.6749	0.6353	0.6029
10.0	0.7343	0.7167	0.6985	0.6807	0.6433	0.6132
20.0	0.7411	0.7244	0.7075	0.6910	0.6569	0.6300
30.0	0.7474	0.7315	0.7154	0.7000	0.6683	0.6436
40.0	0.7532	0.7379	0.7226	0.7080	0.6782	0.6552
50.0	0.7586	0.7440	0.7293	0.7153	0.6871	0.6653
60.0	0.7639	0.7497	0.7355	0.7221	0.6952	0.6744
$x_1 = 0.7928$						
0.1	0.7002	0.6791	0.6582	–	–	–
1.0	0.7008	0.6806	0.6595	0.6383	0.5923	–
5.0	0.7043	0.6847	0.6645	0.6443	0.6012	0.5637
10.0	0.7085	0.6896	0.6702	0.6510	0.6107	0.5770
20.0	0.7159	0.6983	0.6803	0.6627	0.6264	0.5971
30.0	0.7227	0.7062	0.6892	0.6728	0.6392	0.6128
40.0	0.7290	0.7132	0.6971	0.6817	0.6503	0.6258

50.0	0.7348	0.7197	0.7043	0.6897	0.6600	0.6370
60.0	0.7404	0.7257	0.7110	0.6970	0.6688	0.6470

Expanded density uncertainty ($k=2$): $0.7 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T < 373.15 \text{ K}$; $5 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T \geq 373.15 \text{ K}$ and $p=0.1 \text{ MPa}$; $5 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T=463.15 \text{ K}$ and $p=1 \text{ MPa}$; $3 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at other temperature and pressure conditions. Expanded mole fraction uncertainty ($k=2$): $4 \cdot 10^{-4}$. Temperature uncertainty: 0.02 K . Pressure uncertainty: 0.08 MPa .

Figure 4. Density of the binary mixtures as a function of pressure at 323.15 K . (a) n-hexane (1) + n-decane (2): (●) $x_1=0$, (+) $x_1=0.1992$, (■) $x_1=0.3968$, (▲) $x_1=0.4978$, (*) $x_1=0.5957$, (×) $x_1=0.7978$, (◆) $x_1=1$; (b) n-hexane (1) + n-hexadecane (2): (●) $x_1=0$, (+) $x_1=0.1985$, (■) $x_1=0.4136$, (▲) $x_1=0.5007$, (*) $x_1=0.5966$, (×) $x_1=0.7928$, (◆) $x_1=1$. (---) PR EoS, (-.-) PC-SAFT EoS, (-) S-BWR EoS.



Density data for every mixture were also correlated as a function of temperature and pressure through Eq. 18, with an AAD % lower or equal to 0.07% . Fitting parameters as well as the standard deviation (σ) and the absolute average deviation of the fit are reported in Table 8.

Table 8. Fitting parameters of the modified Tammann-Tait equation (Eq. 18), standard deviation of the fit (σ), $D_{\max}\%$, $\text{BIAS}\%$ and $\text{AAD}\%$ for the binary mixtures n-hexane + n-decane and n-hexane + n-hexadecane.

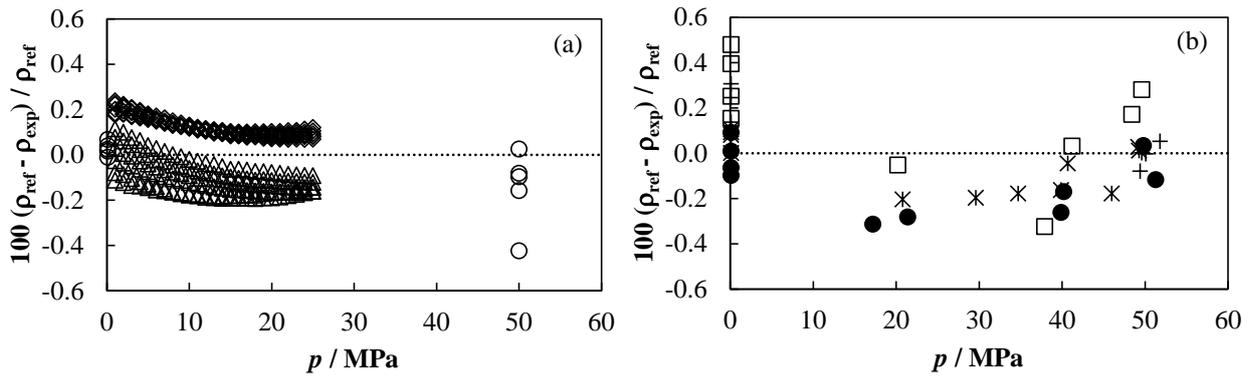
	n-hexane (1) + n-decane (2)				
	$x_1 = 0.1992$	$x_1 = 0.3968$	$x_1 = 0.4978$	$x_1 = 0.5957$	$x_1 = 0.7978$
$A_0 / \text{g} \cdot \text{cm}^{-3}$	0.9786	1.0069	1.0498	1.0402	1.1102
$10^3 \cdot A_1 / \text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$	-1.174	-1.518	-1.93	-1.926	-2.692
$10^6 \cdot A_2 / \text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-2}$	1.625	2.662	3.840	3.925	6.281
$10^9 \cdot A_3 / \text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$	-2.122	-3.226	-4.402	-4.647	-7.185
C	0.08658	0.08725	0.08694	0.08676	0.08783
B_0 / MPa	329.4	319.3	315.3	311.5	311
$B_1 / \text{MPa} \cdot \text{K}^{-1}$	-1.166	-1.142	-1.141	-1.140	-1.175
$10^3 \cdot B_2 / \text{MPa} \cdot \text{K}^{-2}$	1.055	1.038	1.045	1.055	1.119
$10^4 \cdot \sigma / \text{g} \cdot \text{cm}^{-3}$	2.5	3.0	4.5	6.3	5.2
$D_{\max}\%$	0.10	0.11	0.17	0.26	0.25
$\text{Bias}\%$	-0.02	-0.03	0.05	-0.07	-0.02

AAD%	0.02	0.03	0.05	0.07	0.05
	n-hexane (1) + n-hexadecane (2)				
	$x_1 = 0.1985$	$x_1 = 0.4136$	$x_1 = 0.5007$	$x_1 = 0.5966$	$x_1 = 0.7928$
$A_0/\text{g}\cdot\text{cm}^{-3}$	0.9271	0.9440	0.9843	0.9298	0.9881
$10^4\cdot A_1/\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$	-4.158	-6.912	-10.65	-6.747	-13.84
$10^7\cdot A_2/\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-2}$	-5.632	2.659	12.53	1.637	22.36
$10^9\cdot A_3/\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$	0.2505	-0.651	-1.569	-0.6218	-2.813
C	0.08428	0.08615	0.08506	0.08617	0.08757
B_0/MPa	352.2	339.1	330.4	335.0	307.5
$B_1/\text{MPa}\cdot\text{K}^{-1}$	-1.176	-1.141	-1.131	-1.180	-1.103
$10^4\cdot B_2/\text{MPa}\cdot\text{K}^{-2}$	10.25	9.927	9.979	10.72	10.06
$10^4\cdot \sigma/\text{g}\cdot\text{cm}^{-3}$	2.0	2.2	3.3	2.8	3.2
$D_{\max}\%$	0.08	0.10	0.13	0.18	0.08
Bias%	0.01	-0.01	-0.02	0.01	-0.03
AAD%	0.02	0.02	0.03	0.03	0.04

Density values for the n-hexane (1) + n-decane (2) system had been previously reported by Takagi and Teranishi³ at 298.15 K and 0.1, 50 and 100 MPa. Densities of this system were also measured by Quevedo-Nolasco et al.⁴ from (313.15 to 363.15) K up to 25 MPa. Comparison of data reported in the present work with those previously reported was performed, thus in Figure 5(a) deviations from our correlated density values with data from Takagi and Teranishi³ for $x_1=0.2, 0.4, 0.6$ and 0.8 at 298.15 K, as well as with data from Quevedo-Nolasco et al.⁴ for $x_1=0.2185$ and $x_1=0.4968$ from (313.15 to 363.15)K are plotted. These last two compositions were chosen because they are similar to the mixtures studied in this work. The AAD% with data from Takagi and Teranishi³ is 0.09%, whereas with data from Quevedo-Nolasco et al.⁴ is 0.12%. These deviations represent a good agreement with literature, taking into account that there are small differences in the compositions of the compared mixtures.

As regards density values for the n-hexane (1) + n-hexadecane (2) system, they had been previously reported by Dymond et al.⁵ for $x_1=0.2, 0.4, 0.6$ and 0.8 in the temperature range from (298.15 to 373.15)K up to 500 MPa. Correlated density data from this work is compared with data from Dymond et al.⁵ up to 60 MPa in Figure 5(b), both positive and negative deviations were found, the AAD% being 0.15%.

Figure 5. Deviations between correlated density data for the binary mixtures from this work and those from literature. (a) n-hexane (1) + n-decane (2), (\circ) $x_1=0.2, 0.4, 0.6, 0.8$ ³, (\diamond) $x_1=0.2185$ ⁴, (\triangle) $x_1=0.4968$ ⁴; (b) n-hexane (1) + n-hexadecane (2), ($*$) $x_1=0.2$ ⁵, (\bullet) $x_1=0.4$ ⁵, ($+$) $x_1=0.6$ ⁵, (\square) $x_1=0.8$ ⁵.



Density of both binary systems were predicted in the whole experimental (T, p, x) range. The Bias%, AAD% and $D_{\max}\%$ found for density prediction through the different models are presented in Table 9, moreover a comparison of the obtained AADs% is depicted in Figure 6. It can be observed that the SRK EoS yields the poorest prediction for this property for both of the studied systems. The best predictions are obtained by means of both PC-SAFT and S-BWR EoS, with the former slightly better for the system n-hexane + n-hexadecane and the latter slightly better for the system n-hexane + n-decane. Predicted densities through PR, PC-SAFT and S-BWR EoSs are plotted along with the experimental data at $T=323.15$ K in Figure 4. Density predictions through SRK EoS at 323.15 K were not included in Figure 4 due to the high deviation with experimental density values. The SRK predictions vary from 0.57 to 0.63 $\text{g}\cdot\text{cm}^{-3}$ for the system n-hexane + n-decane and from 0.56 to 0.63 $\text{g}\cdot\text{cm}^{-3}$ for the system n-hexane + n-hexadecane. It is worth noting that density calculations through SRK EoS and PR EoS gives rise to crossing points between the isopleths of the ρ - p plot for the system n-hexane + n-decane in the temperature range (278.15 to 348.15)K and for the system n-hexane+n-hexadecane in the temperature range (348.15 to 463.15)K. For pressures higher than the crossover, the density predicted for the heaviest compound (n-decane/n-hexadecane) is lower than the density predicted for the lightest compound (n-hexane). Additionally, at $T=298.15$ K and $T=323.15$ K these two EoSs predict also higher density for the lightest compound (n-hexane) than for the heaviest compound (n-hexadecane).

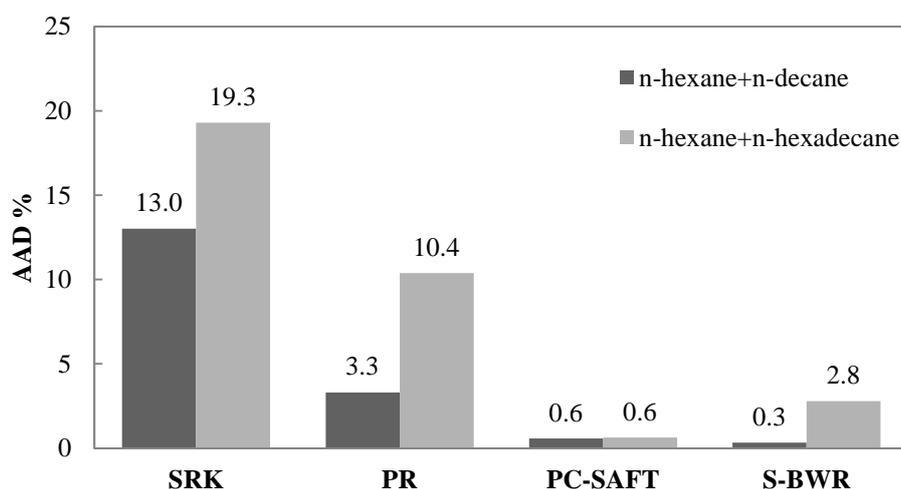
Table 9

Bias%, absolute average deviation (AAD%) and maximum deviation ($D_{\max}\%$) for the prediction of the density of the binary systems n-hexane+n-decane and n-hexane+n-hexadecane in the whole experimental (T, p, x) range through the different EoSs.

	Bias%	AAD%	$D_{\max}\%$
n-hexane + n-decane			
SRK	-13	13	18
PR	-1.8	3.3	9.0
PC-SAFT	0.1	0.6	1.8
S-BWR	-0.1	0.3	1.4
n-hexane + n-hexadecane			
SRK	-19	19	27

PR	-7.4	10	18
PC-SAFT	-0.1	0.6	1.8
S-BWR	-2.6	2.8	4.6

Figure 6. Absolute average deviation (AAD%) for the prediction of the density of the binary systems n-hexane+n-decane and n-hexane+n-hexadecane in the whole experimental (T,p,x) range.



Isothermal compressibility values (κ_T) of the studied binary mixtures were calculated by differentiation of the Tammann-Tait fits, according to the following equation:

$$\kappa_T(T, p) = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (21)$$

The obtained compressibility values are presented in Tables 10 and 11. This property decreases with pressure and increases with temperature, thus the trends with temperature and pressure are opposite to those of density. The maximum variation of isothermal compressibility values under the studied temperature and pressure conditions for every of the studied binary mixtures is between 72% and 89% of the maximum value of this property. Moreover, κ_T values for both binary systems are depicted in Figure 7 at 323.15 K, it can be observed that this property decreases with the carbon number of the n-alkanes from n-hexane to n-hexadecane, therefore the compressibility is higher for the mixtures n-hexane + n-decane than for the mixtures n-hexane + n-hexadecane when compared at the same n-hexane mole fraction.

Table 10

Isothermal compressibility values, $10^3 \kappa_T$ (MPa^{-1}), for the binary system n-hexane (1) + n-decane (2).

T/K

p/MPa	278.15	298.15	323.15	348.15	373.15	423.15	463.15
	$x_1=0$						
1.00	0.94	1.07	1.29	1.56	1.92	3.04	–
5.00	0.90	1.03	1.22	1.46	1.77	2.69	3.79
10.00	0.86	0.97	1.14	1.36	1.62	2.36	3.17
20.00	0.79	0.88	1.02	1.19	1.39	1.90	2.40
30.00	0.73	0.81	0.92	1.06	1.21	1.59	1.94
40.00	0.68	0.75	0.84	0.95	1.08	1.38	1.64
50.00	0.63	0.69	0.78	0.87	0.98	1.21	1.42
	$x_1=0.1992$						
1.00	0.99	1.13	1.36	1.66	–	–	–
5.00	0.95	1.08	1.29	1.55	1.89	2.94	–
10.00	0.90	1.02	1.20	1.43	1.72	2.55	3.52
20.00	0.83	0.92	1.07	1.25	1.46	2.03	2.61
30.00	0.76	0.84	0.97	1.11	1.28	1.69	2.09
40.00	0.71	0.78	0.88	1.00	1.13	1.45	1.75
50.00	0.66	0.72	0.81	0.91	1.02	1.28	1.50
	$x_1=0.3968$						
1.00	1.05	1.21	1.46	–	–	–	–
5.00	1.01	1.15	1.38	1.68	2.07	3.30	–
10.00	0.96	1.09	1.29	1.54	1.87	2.82	3.98
20.00	0.87	0.98	1.14	1.33	1.57	2.21	2.87
30.00	0.80	0.89	1.02	1.18	1.36	1.82	2.26
40.00	0.74	0.82	0.93	1.05	1.20	1.55	1.87
50.00	0.69	0.76	0.85	0.95	1.07	1.35	1.60
	$x_1=0.4978$						
1.00	1.09	1.26	1.54	–	–	–	–
5.00	1.04	1.20	1.44	1.76	2.20	3.60	–
10.00	0.99	1.13	1.34	1.62	1.97	3.05	4.38
20.00	0.90	1.01	1.18	1.39	1.64	2.34	3.08
30.00	0.82	0.92	1.05	1.22	1.41	1.91	2.39
40.00	0.76	0.84	0.95	1.09	1.24	1.61	1.96
50.00	0.71	0.77	0.87	0.98	1.11	1.40	1.67
	$x_1=0.5957$						
1.00	1.13	1.31	1.60	–	–	–	–
5.00	1.08	1.24	1.50	1.84	2.31	3.85	–
10.00	1.02	1.17	1.39	1.68	2.06	3.22	4.66
20.00	0.92	1.04	1.22	1.44	1.71	2.44	3.22
30.00	0.84	0.94	1.08	1.25	1.46	1.97	2.48
40.00	0.78	0.86	0.98	1.12	1.28	1.66	2.03
50.00	0.72	0.79	0.89	1.01	1.14	1.44	1.72
	$x_1=0.7978$						
1.00	1.23	1.44	1.79	–	–	–	–
5.00	1.17	1.36	1.67	2.09	2.67	4.71	–
10.00	1.10	1.27	1.54	1.89	2.35	3.81	5.66
20.00	0.99	1.12	1.33	1.59	1.90	2.78	3.71
30.00	0.90	1.01	1.17	1.37	1.61	2.21	2.79
40.00	0.83	0.92	1.05	1.21	1.39	1.84	2.25
50.00	0.76	0.84	0.95	1.08	1.23	1.58	1.90
	$x_1=1$						
1.00	1.36	1.62	2.08	–	–	–	–
5.00	1.29	1.52	1.91	2.46	3.27	6.34	–
10.00	1.21	1.41	1.74	2.19	2.80	4.84	7.48
20.00	1.07	1.23	1.48	1.79	2.19	3.32	4.52
30.00	0.97	1.10	1.29	1.53	1.81	2.55	3.29
40.00	0.88	0.99	1.15	1.33	1.55	2.08	2.60
50.00	0.81	0.90	1.03	1.18	1.35	1.76	2.17

Expanded isothermal compressibility uncertainty ($k=2$) $\leq 1.1\%$

Table 11

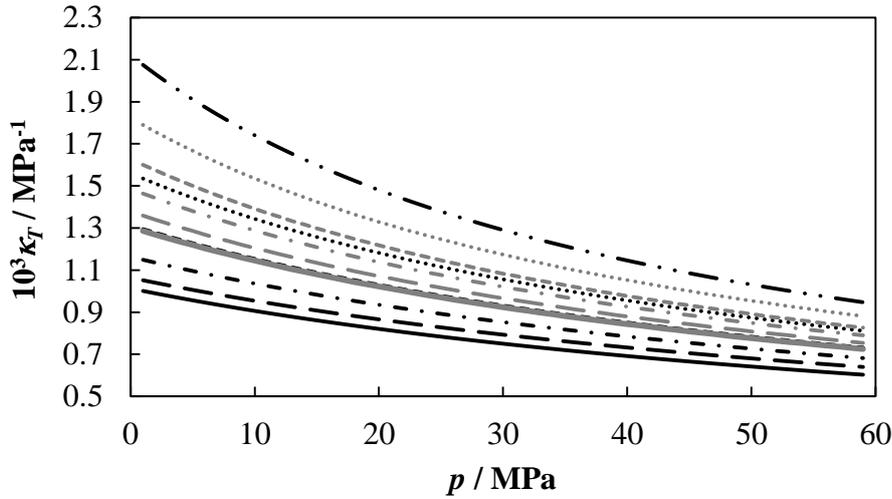
Isothermal compressibility values, $10^3 \kappa_T$ (MPa^{-1}), for the binary system n-hexane (1) + n-hexadecane (2).

p/MPa	T/K					
	298.15	323.15	348.15	373.15	423.15	463.15
	$x_1=0$					
1.00	0.86	1.00	1.18	1.40	2.03	2.76
5.00	0.82	0.96	1.12	1.32	1.86	2.45
10.00	0.79	0.91	1.05	1.22	1.68	2.15
20.00	0.72	0.82	0.94	1.07	1.41	1.73
30.00	0.67	0.75	0.85	0.96	1.22	1.45
40.00	–	0.69	0.77	0.86	1.07	1.25
50.00	–	0.64	0.71	0.79	0.96	1.11
	$x_1=0.1985$					
1.00	0.90	1.05	1.24	1.48	2.16	–
5.00	0.87	1.01	1.18	1.39	1.98	–
10.00	0.83	0.95	1.11	1.29	1.79	2.31
20.00	0.76	0.87	0.99	1.14	1.50	1.86
30.00	0.70	0.79	0.90	1.02	1.30	1.57
40.00	0.65	0.73	0.82	0.92	1.15	1.35
50.00		0.68	0.76	0.84	1.03	1.19
	$x_1=0.4136$					
1.00	0.98	1.15	1.37	1.64	–	–
5.00	0.94	1.10	1.29	1.54	2.23	3.06
10.00	0.90	1.04	1.21	1.42	2.00	2.64
20.00	0.82	0.94	1.07	1.24	1.66	2.09
30.00	0.75	0.85	0.97	1.10	1.42	1.73
40.00	0.70	0.78	0.88	0.99	1.25	1.48
50.00	0.65	0.73	0.81	0.90	1.11	1.30
	$x_1=0.5007$					
1.00	1.03	1.22	1.46	–	–	–
5.00	0.99	1.16	1.38	1.65	2.45	3.43
10.00	0.94	1.09	1.28	1.52	2.17	2.91
20.00	0.85	0.98	1.13	1.31	1.77	2.24
30.00	0.78	0.89	1.01	1.15	1.50	1.83
40.00	0.72	0.81	0.92	1.03	1.31	1.56
50.00	0.67	0.75	0.84	0.94	1.16	1.35
	$x_1=0.5966$					
1.00	1.09	1.29	1.57	–	–	–
5.00	1.04	1.23	1.47	1.78	2.68	3.75
10.00	0.98	1.15	1.36	1.63	2.35	3.15
20.00	0.89	1.03	1.19	1.39	1.90	2.39
30.00	0.82	0.93	1.06	1.22	1.60	1.94
40.00	0.75	0.85	0.96	1.09	1.38	1.64
50.00	0.70	0.78	0.88	0.98	1.22	1.42
	$x_1=0.7928$					
1.00	1.27	1.54	1.89	–	–	–
5.00	1.21	1.44	1.75	2.16	3.44	–
10.00	1.14	1.34	1.61	1.95	2.93	4.11
20.00	1.02	1.18	1.38	1.63	2.27	2.94
30.00	0.92	1.06	1.21	1.40	1.87	2.31
40.00	0.84	0.96	1.08	1.23	1.59	1.91
50.00	0.78	0.87	0.98	1.10	1.38	1.63
	$x_1=1$					
1.00	1.62	2.08	–	–	–	–

5.00	1.52	1.91	2.46	3.27	6.34	–
10.00	1.41	1.74	2.19	2.80	4.84	7.48
20.00	1.23	1.48	1.79	2.19	3.32	4.52
30.00	1.10	1.29	1.53	1.81	2.55	3.29
40.00	0.99	1.15	1.33	1.55	2.08	2.60
50.00	0.90	1.03	1.18	1.35	1.76	2.17

Expanded isothermal compressibility uncertainty ($k=2$) $\leq 1.0\%$

Figure 7. Isothermal compressibility (κ_T) of the binary mixtures n-hexane (1) + n-decane (2) (grey lines) and n-hexane (1) + n-hexadecane (2) (black lines) at 323.15 K. (—) $x_1=0$, (— —) $x_1=0.2$, (-·-) $x_1=0.4$, (---) $x_1=0.6$, (···) $x_1=0.8$, (— · —) $x_1=1$.



Excess molar volumes of the studied binary systems were calculated according to the following equation:

$$V^E = \frac{x_1 M_1 + (1-x_1) M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{(1-x_1) M_2}{\rho_2} \right) \quad (22)$$

where x_1 is the mole fraction of the component 1 of the mixture, M_1 and M_2 are the molecular weights of components 1 and 2 of the mixture, respectively. ρ , ρ_1 and ρ_2 are density values of the mixture, component 1 and component 2, respectively.

Values of the excess volume for both mixtures are presented in Tables 12 and 13. Negative excess volumes were found for both systems in the whole composition, temperature and pressure range. For the system n-hexane + n-decane the maximum negative value of this property is generally found for the equimolar mixture ($x_1=0.4978$), being the highest value $-3.25 \text{ cm}^3 \text{ mol}^{-1}$ found at this composition at 463.15 K and 5 MPa. Katzenski and Schneider²⁹ had previously reported excess volumes of this system for the equimolar composition at 298.15 K and pressures up to 200 MPa. Comparison of the reported excess volumes with the ones reported in this work from 10 to 50 MPa yielded an absolute average deviation of $0.02 \text{ cm}^3 \text{ mol}^{-1}$. As regards the system n-hexane + n-hexadecane, the deviations from ideality are asymmetrical, i.e. the maximum negative value of the

excess volume is generally found in the studied temperature and pressure range at $x_1=0.5966$, being its maximum negative value of $-7.65 \text{ cm}^3\text{mol}^{-1}$ at 463.15 K, 5 MPa and $x_1=0.7928$. Excess volumes for both binary systems are presented in Figure 8 at 323.15 K and 463.15 K. It can be observed that excess volumes are more negative for the system n-hexane + n-hexadecane than for the system n-hexane + n-decane. This property becomes more negative with temperature rise and less negative with pressure rise. These observations on excess volume of the studied binary systems are in agreement with results previously reported for different n-alkane mixtures by Lepori et al.³⁰, Katzenski and Schneier²⁹ and Trejo-Rodríguez and Paterson³¹, among others. Thus Lepori et al.³⁰, after study of alkane binary mixtures containing n-heptane at ambient pressure stand that excess volume decreases with the increase of the hydrocarbon size, at the same time that the minimum shifts to larger concentrations of the shorter alkane. Moreover Katzenski and Schneider²⁹ reported that the excess volume become less negative when increasing pressure. As concerns Trejo-Rodríguez and Paterson³¹, they discussed the excess volume of the system n-hexane + n-hexadecane at ambient pressure, stating that the skewing of this property towards the n-hexane is not only related with the difference in chain length between both alkanes, but also with the large free volume of n-hexane and the orientational order of n-hexadecane. Therefore, these last authors³¹ conclude that the excess volume is large and with the minimum displaced towards the region of high concentration of the lighter alkane when the free-volume contribution is significant, e.g. n-pentane + n-hexadecane, but it is small and symmetric when the free volume contribution is negligible, e.g. n-decane + n-hexadecane.

Table 12

Excess volume, V^E ($\text{cm}^3\text{mol}^{-1}$), for the binary system n-hexane (1) + n-decane (2).

p/MPa	T/K						
	278.15	298.15	323.15	348.15	373.15	423.15	463.15
$x_1=0.1992$							
0.1	-0.13	-0.05	-0.29	–	–	–	–
1.0	-0.12	-0.10	-0.29	-0.33	-0.48	-1.22	–
5.0	-0.09	-0.08	-0.25	-0.28	-0.39	-0.86	-1.63
10.0	-0.08	-0.07	-0.22	-0.24	-0.32	-0.61	-0.98
20.0	-0.08	-0.07	-0.19	-0.20	-0.26	-0.39	-0.56
30.0	-0.07	-0.05	-0.14	-0.16	-0.22	-0.29	-0.42
40.0	-0.05	-0.03	-0.11	-0.13	-0.18	-0.23	-0.33
50.0	-0.02	-0.03	-0.10	-0.12	-0.14	-0.16	-0.25
60.0	-0.03	-0.01	-0.09	-0.10	-0.10	-0.14	-0.27
$x_1=0.3968$							
0.1	-0.16	-0.12	-0.36	–	–	–	–
1.0	-0.16	-0.21	-0.35	-0.54	-0.93	-2.10	–
5.0	-0.15	-0.18	-0.32	-0.47	-0.77	-1.50	-3.10
10.0	-0.14	-0.17	-0.29	-0.42	-0.64	-1.13	-1.98
20.0	-0.10	-0.13	-0.22	-0.34	-0.50	-0.78	-1.23
30.0	-0.10	-0.12	-0.17	-0.27	-0.40	-0.63	-0.95
40.0	-0.09	-0.14	-0.15	-0.24	-0.36	-0.55	-0.81
50.0	-0.05	-0.13	-0.14	-0.22	-0.33	-0.49	-0.72
60.0	-0.06	-0.11	-0.12	-0.20	-0.28	-0.43	-0.72

	$x_1 = 0.4978$						
0.1	-0.22	-0.15	-0.32	–	–	–	–
1.0	-0.22	-0.19	-0.32	-0.53	-0.85	-2.22	–
5.0	-0.21	-0.17	-0.29	-0.46	-0.66	-1.55	-3.25
10.0	-0.19	-0.14	-0.23	-0.39	-0.55	-1.12	-1.93
20.0	-0.17	-0.12	-0.18	-0.30	-0.44	-0.76	-1.09
30.0	-0.14	-0.09	-0.13	-0.23	-0.34	-0.57	-0.80
40.0	-0.12	-0.08	-0.11	-0.19	-0.28	-0.46	-0.66
50.0	-0.11	-0.07	-0.10	-0.17	-0.25	-0.39	-0.59
60.0	-0.09	-0.06	-0.08	-0.15	-0.22	-0.33	-0.59
	$x_1 = 0.5957$						
0.1	-0.17	-0.12	-0.33	–	–	–	–
1.0	-0.17	-0.19	-0.32	-0.51	-0.79	-2.14	–
5.0	-0.15	-0.16	-0.28	-0.43	-0.62	-1.42	-3.17
10.0	-0.13	-0.13	-0.23	-0.37	-0.49	-0.98	-1.80
20.0	-0.10	-0.09	-0.17	-0.29	-0.37	-0.60	-0.95
30.0	-0.08	-0.07	-0.12	-0.21	-0.28	-0.42	-0.65
40.0	-0.07	-0.06	-0.10	-0.17	-0.21	-0.31	-0.49
50.0	-0.06	-0.05	-0.08	-0.14	-0.17	-0.24	-0.40
60.0	-0.03	-0.03	-0.06	-0.11	-0.14	-0.19	-0.37
	$x_1 = 0.7978$						
0.1	-0.10	-0.01	-0.25	–	–	–	–
1.0	-0.12	-0.18	-0.23	-0.44	-0.71	-1.93	–
5.0	-0.11	-0.18	-0.21	-0.36	-0.55	-1.26	-2.77
10.0	-0.09	-0.15	-0.18	-0.30	-0.44	-0.93	-1.49
20.0	-0.08	-0.12	-0.13	-0.23	-0.34	-0.60	-0.84
30.0	-0.07	-0.10	-0.09	-0.18	-0.28	-0.45	-0.62
40.0	-0.06	-0.10	-0.08	-0.15	-0.24	-0.39	-0.50
50.0	-0.04	-0.09	-0.07	-0.13	-0.22	-0.40	-0.45
60.0	-0.03	-0.08	-0.06	-0.12	-0.19	-0.39	-0.41

Expanded uncertainty of the excess volume ($k=2$): 0.01 - 0.16 cm³mol⁻¹

Table 13

Excess volume, V^E (cm³mol⁻¹), for the binary system n-hexane (1) + n-hexadecane (2).

p/MPa	T/K					
	298.15	323.15	348.15	373.15	423.15	463.15
	$x_1 = 0.1985$					
0.1	-0.21	-0.52	–	–	–	–
1.0	-0.26	-0.54	-0.67	-0.95	-2.07	–
5.0	-0.22	-0.48	-0.62	-0.83	-1.54	-3.18
10.0	-0.17	-0.42	-0.55	-0.71	-1.17	-2.16
20.0	-0.12	-0.35	-0.46	-0.58	-0.80	-1.37
30.0	-0.08	-0.29	-0.38	-0.47	-0.59	-1.02
40.0	–	-0.25	-0.33	-0.39	-0.46	-0.84
50.0	–	-0.23	-0.29	-0.34	-0.38	-0.73
60.0	–	-0.23	-0.28	-0.31	-0.33	-0.68
	$x_1 = 0.4136$					
0.1	-0.41	-0.80	–	–	–	–
1.0	-0.49	-0.81	-1.30	-1.73	-3.85	–
5.0	-0.45	-0.72	-1.16	-1.48	-2.91	-5.66

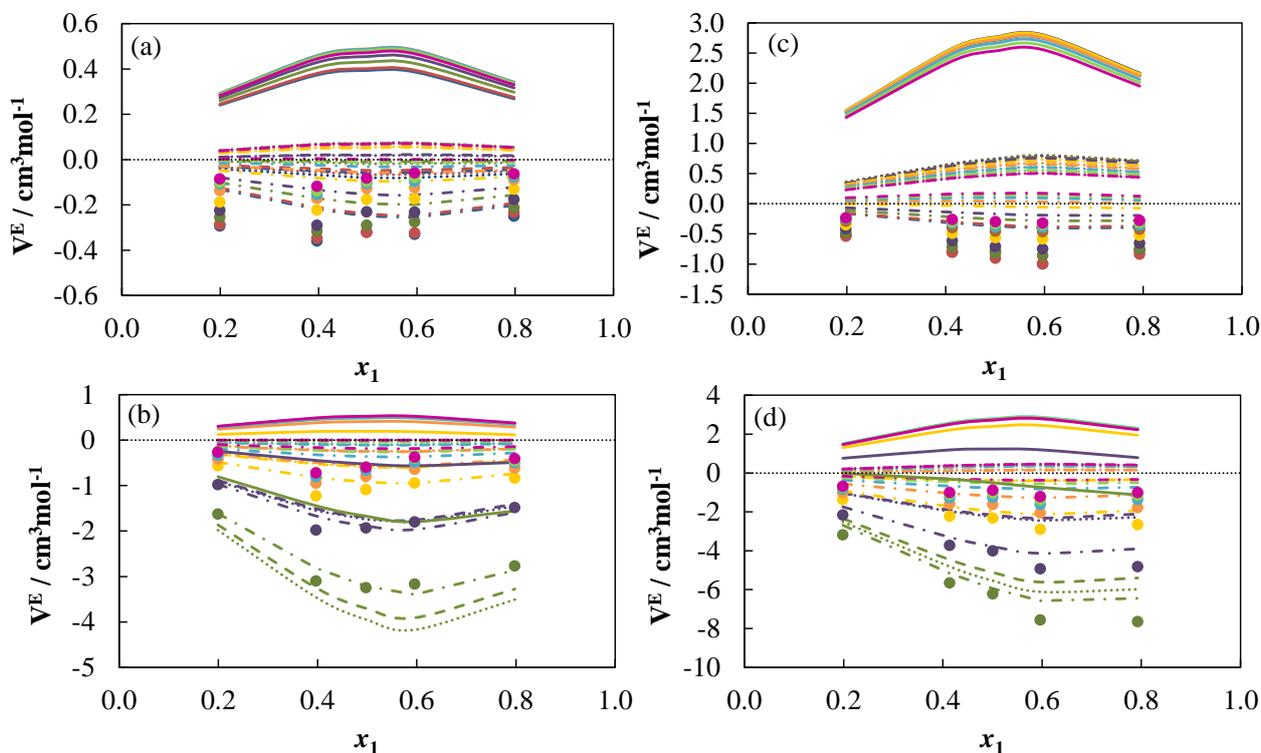
10.0	-0.37	-0.62	-1.02	-1.25	-2.22	-3.73
20.0	-0.28	-0.49	-0.84	-0.97	-1.48	-2.23
30.0	-0.21	-0.40	-0.70	-0.80	-1.09	-1.60
40.0	–	-0.32	-0.60	-0.68	-0.87	-1.27
50.0	–	-0.30	-0.55	-0.63	-0.74	-1.11
60.0	–	-0.26	-0.50	-0.58	-0.65	-1.01
$x_1=0.5007$						
0.1	-0.48	-0.79	–	–	–	–
1.0	-0.59	-0.91	-1.28	-1.85	-4.31	–
5.0	-0.52	-0.82	-1.10	-1.55	-3.19	-6.22
10.0	-0.44	-0.71	-0.93	-1.28	-2.38	-4.01
20.0	-0.33	-0.56	-0.73	-0.99	-1.56	-2.32
30.0	-0.26	-0.46	-0.59	-0.80	-1.14	-1.62
40.0	–	-0.39	-0.49	-0.68	-0.89	-1.26
50.0	–	-0.33	-0.42	-0.60	-0.72	-1.04
60.0	–	-0.30	-0.36	-0.54	-0.61	-0.89
$x_1=0.5966$						
0.1	-0.52	-1.00	–	–	–	–
1.0	-0.61	-1.00	-1.42	-2.12	-4.91	–
5.0	-0.55	-0.86	-1.23	-1.76	-3.60	-7.57
10.0	-0.48	-0.75	-1.08	-1.49	-2.73	-4.94
20.0	-0.37	-0.58	-0.86	-1.14	-1.83	-2.90
30.0	-0.29	-0.47	-0.69	-0.92	-1.37	-2.05
40.0	–	-0.39	-0.59	-0.78	-1.11	-1.62
50.0	–	-0.35	-0.52	-0.68	-0.94	-1.37
60.0	–	-0.32	-0.47	-0.62	-0.84	-1.22
$x_1=0.7928$						
0.1	-0.45	-0.77	–	–	–	–
1.0	-0.58	-0.84	-1.26	-1.95	-5.09	–
5.0	-0.53	-0.75	-1.10	-1.62	-3.66	-7.65
10.0	-0.46	-0.65	-0.94	-1.33	-2.70	-4.82
20.0	-0.36	-0.52	-0.74	-1.00	-1.71	-2.65
30.0	-0.28	-0.42	-0.60	-0.80	-1.22	-1.78
40.0	–	-0.36	-0.51	-0.67	-0.96	-1.36
50.0	–	-0.31	-0.44	-0.59	-0.80	-1.14
60.0	–	-0.28	-0.39	-0.53	-0.70	-1.01

Expanded uncertainty of the excess volume ($k=2$): $0.01 - 0.36 \text{ cm}^3\text{mol}^{-1}$

Figure 8 shows also predictions for the different models analyzed in this work for the excess volume of the binary systems. It can be observed that prediction of this property improves as V^E increases, that is for higher temperatures and lower pressures. It is worth mentioning that the worst prediction for this property is given by S-BWR model, although density prediction is quite satisfactory through this EoS. Surprisingly, V^E predictions through SRK and PR are better than S-BWR, even though their density predictions are poorer. The best performance in terms of excess volume prediction is obtained by means of SRK, PR and PC-SAFT EoSs, with slightly better results from PC-SAFT.

Figure 8. Excess volume for the binary systems (a,b) n-hexane (1) + n-decane (2) and (c,d) n-hexane (1) + n-hexadecane (2) at (a,c) 323.15 K and (b,d) 463.15 K. (●) 0.1 MPa, (●) 1 MPa, (●)

5 MPa, (●) 10 MPa, (●) 20 MPa, (●) 30 MPa, (●) 40 MPa, (●) 50 MPa and (●) 60 MPa. (···) SRK EoS, (---) PR EoS, (-.-) PC-SAFT EoS, (-) S-BWR EoS.



5. CONCLUSIONS

Density, isothermal compressibility and excess volumes were reported for the binary systems n-hexane + n-decane and n-hexane + n-hexadecane up to 60 MPa in the whole composition range from (278.15 to 463.15)K and from (298.15 to 463.15)K, respectively. Higher density values are obtained for n-hexane + n-hexadecane, whereas higher compressibility values are obtained for the system n-hexane + n-decane when compared at the same temperature, pressure and mole fractions. As concerns excess volume, negative values of this property were found for both binary systems, being more negative for the system n-hexane + n-hexadecane. Moreover, excess volume curves for the system n-hexane + n-decane are rather symmetric with composition, whereas for the n-hexane + n-hexadecane system the minimum on excess volume is slightly displaced towards higher n-hexane molar fraction.

As concerns modeling, it was found that PC-SAFT and S-BWR are the models that yield better prediction for the density of the binary systems, with AADs lower than 1 and 3%, respectively. However, regarding prediction of the excess volume, it was found that S-BWR leads to the poorest performance of the studied EoS, the best predictions being obtained through PC-SAFT EoS.

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