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Density and compressibility of multicomponent n-alkane mixtures up to 463 K and 140 MPa

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Abstract

Density measurements of two ternary alkane mixtures (methane/n-butane/n-decane and methane/n-butane/n-dodecane) and two multicomponent mixtures composed of methane/n-butane/n-octane/n-dodecane/n-hexadecane/n-eicosane were performed in the temperature range from (278.15 to 463.15)K and pressures up to 140 MPa. The isothermal compressibility values of these mixtures were obtained by differentiation from a Tait type fitting of experimental densities as a function of temperature and pressure. Excess volume of the studied mixtures was also determined. Four different equations of state, i.e. Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT), and Soave-Benedict-Webb-Rubin (Soave-BWR) were used for predicting the experimental density values as well as the excess volumes.

Keywords: density, compressibility, alkane mixture, pressure, excess volume

1. Introduction

The global demand for oil and gas is expected to increase in the foreseeable future alongside the declining conventional oil and gas resources. This has driven the oil and gas industry towards the exploration of deeper formations, which are characterized by more extreme temperature and pressure conditions than conventional reservoirs. Safe exploitation of these formations requires a multidisciplinary effort, including a better understanding and description of the reservoir fluids. Among the thermophysical characterization of the high pressure-high temperature (HPHT) reservoir fluids, accurate description of density and isothermal compressibility is indispensable. Density is a key property determining the volumetric behaviour of the reservoir fluids. It is employed in the estimation of oil and gas resources, and also useful for calculation of the pressure-depth relation in the reservoir.¹ Density values are also needed to perform an accurate determination of the interfacial tension.^{2,3} In addition, the compressibility of the reservoir fluids is one of the driving factors in the primary reservoir production and it is used in the determination of the oil recovery factor.⁴

There are limited volumetric data of asymmetric hydrocarbon mixtures under HPHT conditions in open literature. Reamer et al.⁵⁻⁷ published data on the volumetric behavior of the ternary mixtures methane/propane/n-decane and methane/n-butane/n-decane. Snyder et al.⁸ measured density of a ternary mixture composed of n-decane/n-tetradecane/n-hexadecane. Pečar and Doleček⁹ determined

density of the ternary system n-pentane/n-hexane/n-heptane. Fenghour et al.^{10, 11} reported densities of the ternary mixtures n-butane/n-heptane/n-hexadecane and methane/n-butane/n-hexadecane as well as of the quaternary mixture methane/n-butane/n-heptane/n-hexadecane. Also the density of the ternary system propane/n-butane/isobutane was determined by Miyamoto et al.¹² Parrish¹³ provided density data of the ternary mixture ethane/propane/n-butane and Kariznovi et al.¹⁴ reported density values of the ternary system methane/n-decane/n-tetradecane.

Using well-defined synthetic mixtures as model reservoir fluids provides an approach to studying the contribution of the different compounds to the final reservoir properties while avoiding the challenging sampling process of the actual reservoir fluids. Although data for these synthetic systems cannot replace the PVT study of real reservoir fluids, they can provide an insight on the behaviour of these fluids, and contribute to testing and improving the performance of thermodynamic models under HPHT conditions. In addition, synthetic systems present the advantage of a precisely defined composition in contrast to the uncertainties inherent to reservoir fluid characterization. In our recent work¹⁵ we have studied the phase equilibria under high temperature and pressure conditions of four synthetic alkane mixtures which were intended to serve as model systems for real reservoir fluids. These mixtures included a model system for volatile oil and three model systems for gas condensate. The present work is a continuation with focus on the volumetric properties of these model reservoir fluids.

The four synthetic mixtures include two ternary mixtures composed of methane/n-butane/n-decane and methane/n-butane/n-dodecane, and two 6-component mixtures composed of methane/n-butane/n-octane/n-dodecane/n-hexadecane/n-eicosane. The two 6-component mixtures were named the low GOR mixture and the high GOR mixture, respectively, according to the level of gaseous methane component in the mixture. The four mixtures have essentially the same composition as those in our previous work¹⁵. Since the mixtures in this study are prepared in a different batch, there are slight variations in their composition. Except for the low GOR mixture which mimics volatile oil, all the other three mixtures behave as gas condensate in the studied temperature range. Density of these systems was determined at temperatures up to 463.15 K and pressures up to 140 MPa. Isothermal compressibility and excess volumes were also determined from the experimental density data. Several thermodynamic models, including Soave-Redlich-Kwong¹⁶ (SRK), Peng-Robinson¹⁷ (PR), Perturbed Chain Statistical Associating Fluid Theory¹⁸ (PC-SAFT) and Soave-Benedict-Webb-Rubin¹⁹ (SBWR) were finally used to predict the density and excess volume of the measured systems.

2. Materials and methods

2.1. Materials

The materials used in this work along with their purity are presented in Table 1. The liquid chemicals at ambient conditions were degassed at least for 3600 s by means of an ultrasonic bath Branson 1510 DTH prior to their use.

Table 1. Provider and mole fraction purity of the chemicals

Chemical name	Provider	Purity*
methane	AGA gas	0.999995
n-butane	AGA gas	0.9995
n-octane	Sigma-Aldrich	0.994 ^a
n-decane	Sigma-Aldrich	0.998 ^a
n-dodecane	Sigma-Aldrich	0.993 ^a
n-hexadecane	Sigma-Aldrich	0.994 ^a
n-eicosane	Sigma-Aldrich	0.996 ^a

* Given by the manufacturer

^aGas chromatography

Mixtures were prepared inside a high pressure cylinder (sample cylinder) which is divided into two parts by means of an inner piston. One side of it was filled with water, which was used as a hydraulic fluid, whereas the other side was filled with the sample. The sample side was first evacuated prior to the filling process. For the preparation of the ternary mixtures methane/n-butane/n-decane and methane/n-butane/n-dodecane, n-decane (or n-dodecane) was first added volumetrically to the evacuated sample cylinder by using a burette (standard uncertainty 0.01 cm³), after n-butane and methane were subsequently added gravimetrically by using an analytical balance Mettler-Toledo PR 1203 which has a standard uncertainty of 0.001 g. For the preparation of the 6-compound mixtures, first n-eicosane was dissolved in the ternary liquid mixture composed of n-octane, n-dodecane and n-hexadecane. Afterwards this 4-compound liquid mixture was volumetrically added to the sample cylinder through a burette (standard uncertainty 0.01 cm³), and finally n-butane and n-methane were added gravimetrically to the mixture. Once all the mixture compounds had been added to the sample side of the high pressure cylinder, the pressure of the sample was increased to a pressure at least 3 MPa higher than the saturation pressure of the mixture, this was done by using a syringe pump (Teledyne Isco 100 DX) connected to the water side of the sample cylinder. After the pressure was increased to the desired value, the cylinder was rocked in order to achieve the homogenization of the prepared mixture. Inside the sample side of the high pressure cylinder there is a stainless-steel ball which helps the mixing of the mixture when rocking. The composition of the mixtures studied in this work is given in Table 2.

Table 2. Composition in mole fraction^a of the ternary (C₁-C₄-C₁₀, C₁-C₄-C₁₂) and multicomponent (low GOR and high GOR) mixtures studied in this work.

Compound	C ₁ -C ₄ -C ₁₀	C ₁ -C ₄ -C ₁₂	Low GOR	High GOR
methane	0.8099	0.8494	0.6969	0.9001
n-butane	0.1400	0.1004	0.1213	0.0301
n-octane	–	–	0.0708	0.0299
n-decane	0.0501	–	–	–
n-dodecane	–	0.0502	0.0504	0.0199
n-hexadecane	–	–	0.0303	0.0150
n-eicosane	–	–	0.0303	0.0050

^aExpanded mole fraction uncertainty $U(x)$ ($k=2$): $6 \cdot 10^{-4}$

2.2. Density measurements

The density of the mixtures was measured by using a vibrating tube densitometer Anton Paar DMA HPM. The densitometer is connected to a pressure line comprised of a manual pressure generator (HiP 37-6-30) and a pressure transducer SIKA type P which measures the pressure up to 150 MPa with a 0.05 % FS uncertainty. The measuring cell of the densitometer is thermostated through a liquid circulator bath Julabo PRESTO A30. The temperature is measured by means of a Pt100 inserted inside the measurement cell with an uncertainty of ± 0.02 K. The oscillation period of the vibrating tube densitometer is displayed with seven significant figures. An schematic of the experimental setup can be found elsewhere.²⁰

In order to keep the prepared mixtures in the single phase conditions, they were isobarically transferred to the evacuated densitometer by using a syringe pump (Teledyne Isco 100 DX) connected to the sample cylinder. The transfer of the sample was carried out at a pressure around 3 MPa higher than the saturation pressure of the mixture.¹⁵ A buffer cylinder is located in the downstream of the densitometer where a certain volume (around 30 cm³) of the mixture was purged in order to assure that the composition of sample in the densitometer measuring cell was the same as the one prepared in the sample cylinder.

The calibration of the densitometer was performed following a modification of the Lagourette et al.²¹ method, in an analogous way to that described by Comuñas et al.²² by using as reference fluids vacuum, Milli-Q water and n-dodecane. Specific details about the calibration process are given elsewhere²⁰. The density measurements of the ternary and multicomponent mixtures were performed in this work from (278.15 to 463.15)K at pressures up to 140 MPa. The minimum pressures of the measurements were set to values higher than the saturation pressures of the mixtures, being 40 MPa for the C₁-C₄-C₁₀, C₁-C₄-C₁₂ and low GOR systems and 60 MPa for the high GOR system. The uncertainty of density measurements by using a vibrating tube densitometer Anton Paar DMA HPM has been rigorously analyzed by Segovia et al.²³ In this work the expanded ($k=2$) uncertainty of the density measurements is considered to be $7 \cdot 10^{-4}$ g·cm⁻³ at $T < 373.15$ K, and $3 \cdot 10^{-3}$ g·cm⁻³ in other temperature conditions.

The density measurements were performed in the temperature range from (278.15 to 463.15)K and pressures from (40 to 140)MPa for the C₁-C₄-C₁₀ system. The system C₁-C₄-C₁₂ as well as the low GOR system were studied in the temperature range from (298.15 to 463.15)K and pressures from (40 to 140)MPa. Finally the density of the high GOR system was studied from (298.15 to 463.15)K and pressures from (60 to 140)MPa. Taken into account the saturation pressures determined for these ternary and multicomponent mixtures in a previous study¹⁵ it can be stated that under the experimental conditions the low GOR system is liquid whereas the C₁-C₄-C₁₀, C₁-C₄-C₁₂ and the high GOR systems are gas.

2.3. Modelling

Two cubic equations of state (EoSs) were used in this work to model the density and excess volume data, Soave-Redlich-Kwong¹⁶ (SRK), and Peng-Robinson¹⁷ (PR). The prediction of these two properties was also performed through two non-cubic EoSs, Perturbed Chain Statistical Associating Fluid Theory¹⁸ (PC-SAFT) and Soave-Benedict-Webb-Rubin¹⁹ (SBWR). The simplified version of PC-SAFT was used in the calculations, as described by von Solms et al.²⁴

The pure compound parameters used in the modelling of the studied mixtures are presented in table 3, whereas the binary interaction parameters given in Table 4 were previously regressed by Yan et al.²⁵ from existing VLE data on binary systems. The same pure compound and binary interaction parameters have been recently used¹⁵ to predict the saturation pressures of the alkane mixtures studied in this work.

Table 3. Pure compound parameters used in the different EoSs analyzed in this work. Critical temperature (T_c), critical pressure (p_c), acentric factor (ω), segment diameter (σ), segment energy (ε), Boltzmann constant (k) and chain length (m).

	methane	n-butane	n-octane	n-decane	n-dodecane	n-hexadecane	n-eicosane
T_c / K^*	190.56 [‡]	425.12 [‡]	568.70 [‡]	617.70 [‡]	658.00 [‡]	723.00 [‡]	768.00 [‡]
p_c / MPa^*	4.599 [‡]	3.796 [‡]	2.490 [‡]	2.110 [‡]	1.820 [‡]	1.400 [‡]	1.160 [‡]
ω^*	0.0115	0.2002	0.3996	0.4923	0.5764	0.7174	0.9069
$\sigma / \text{\AA}^\S$	3.7039	3.7086	3.8373	3.8384	3.8959	3.9552	3.9120
$\varepsilon k^{-1} / \text{K}^\S$	150.03	222.88	242.78	243.87	249.21	254.70	251.92
m^\S	1.0000	2.3316	3.8176	4.6627	5.3060	6.6485	8.4092

*DIPPR database²⁶

[§]Gross and Sadowski¹⁸

[‡]Ambrose and Tsonopoulos²⁷

[†]Tsonopoulos and Tan²⁸

Table 4. Binary interaction parameters (k_{ij}) of the pairs methane/n-alkane taken from Yan et al.²⁵

k_{ij}	SRK	PR	PC-SAFT	SBWR
methane/n-butane	0.0100	0.0168	0.0041	-0.0044
methane/n-octane	0.0410	0.0451	0.0159	-0.0149
methane/n-decane	0.0411	0.0409	0.0172	-0.0311
methane/n-dodecane	0.0442	0.0500	0.0103	-0.0315
methane/n-hexadecane	0.0586	0.0561	0.0189	-0.0441
methane/n-eicosane	0.0534	0.0541	0.0172	-0.0405

3. Results and discussion

In the present work the absolute average deviation (AAD) and standard deviation (σ) were used to compare the experimental data obtained in this work with those from model predictions. The following equations were used:

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

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

where Y_i^{exp} is the value of the experimental property determined in this work, Y_i^{cal} is the calculated value of the same property, N is the number of experimental data points and p is the number of fitting parameters.

3.1. Density

The measured densities for the studied systems are gathered in Table 5. These values are illustrated in Figure 1 as a function of pressure for the different temperatures studied. It can be observed the usual trend of density with pressure and temperature, i.e., it increases with pressure along isotherms whereas it decreases with temperature along isobars. The highest densities were measured for the liquid mixture (low GOR), whereas the density measured for the gas mixtures (C₁-C₄-C₁₀, C₁-C₄-C₁₂, high GOR) is relatively similar when compared under the same pressure and temperature conditions. Specifically an AAD of 1.4% was obtained when comparing the experimental density values of the two ternary mixtures, an AAD of 1.0 % was obtained in the comparison of the density values of the C₁-C₄-C₁₂ and the high GOR mixture and an AAD of 0.6 % was obtained when comparing the density of the C₁-C₄-C₁₀ and the high GOR system. These AAD values show that the three synthetic mixtures selected as a simple model of a gas condensate present relatively similar density values.

Table 5. Density^a, ρ , of the different ternary and multicomponent systems measured in this work in g·cm⁻³ at temperature T and pressure p .

T/K	p/MPa					
	40.0	60.0	80.0	100.0	120.0	140.0
C ₁ -C ₄ -C ₁₀						
278.15	0.4350	0.4637	0.4834	0.4995	0.5134	0.5252
298.15	0.4135	0.4466	0.4685	0.4860	0.5007	0.5131
323.15	0.3874	0.4261	0.4510	0.4702	0.4862	0.4994
348.15	0.3628	0.4066	0.4345	0.4553	0.4725	0.4863
373.15	0.3398	0.3883	0.4187	0.4410	0.4590	0.4732
423.15	0.2998	0.3551	0.3891	0.4136	0.4328	0.4474
463.15	0.2721	0.3303	0.3661	0.3920	0.4129	0.4294
C ₁ -C ₄ -C ₁₂						
298.15	0.3998	0.4376	0.4627	0.4822	0.4984	0.5123

323.15	0.3726	0.4157	0.4436	0.4653	0.4831	0.4981
348.15	0.3479	0.3960	0.4265	0.4496	0.4686	0.4846
373.15	0.3285	0.3808	0.4133	0.4367	0.4563	0.4742
423.15	0.2954	0.3540	0.3888	0.4144	0.4367	0.4562
463.15	0.2728	0.3336	0.3704	0.3982	0.4223	0.4427

Low GOR

298.15	0.5787	0.5988	0.6142	0.6272	0.6385	0.6484
323.15	0.5527	0.5767	0.5946	0.6093	0.6219	0.6329
348.15	0.5303	0.5581	0.5782	0.5944	0.6081	0.6200
373.15	0.5084	0.5400	0.5623	0.5801	0.5950	0.6078
423.15	0.4669	0.5067	0.5338	0.5546	0.5714	0.5857
463.15	0.4369	0.4829	0.5132	0.5360	0.5541	0.5690

High GOR

298.15	—	0.4424	0.4670	0.4855	0.5005	0.5132
323.15	—	0.4226	0.4499	0.4702	0.4865	0.5002
348.15	—	0.4025	0.4320	0.4536	0.4708	0.4853
373.15	—	0.3828	0.4147	0.4384	0.4572	0.4728
423.15	—	0.3475	0.3846	0.4116	0.4326	0.4495
463.15	—	0.3234	0.3637	0.3928	0.4151	0.4329

^aExpanded density uncertainty $U(\rho)$ ($k=2$): $0.7 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at $T < 373.15 \text{ K}$; $3 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ at other temperature conditions; standard temperature uncertainty $u(T)$: 0.02 K ; standard pressure uncertainty $u(p)$: 0.08 MPa .

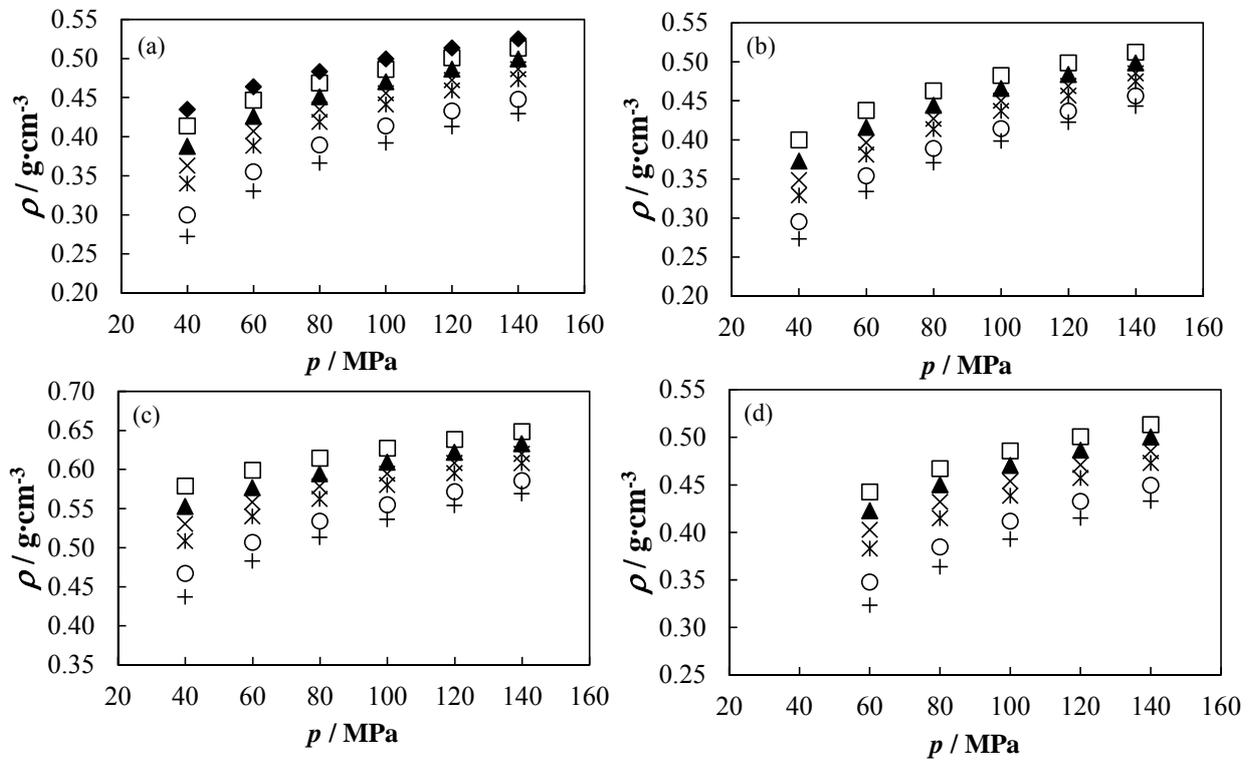


Figure 1. Density, ρ , of the ternary and multicomponent mixtures measured in this work as a function of pressure. (a) C₁-C₄-C₁₀, (b) C₁-C₄-C₁₂, (c) low GOR and (d) high GOR mixtures. (◆) 278.15 K, (□) 298.15 K, (▲) 323.15 K, (×) 348.15 K, (*) 373.15 K, (○) 423.15 K and (+) 463.15 K.

The experimental density data have been correlated for each of the studied systems by means of the following modified Tammann-Tait equation:

$$\rho(T, p) = \frac{\rho(T, p_{ref})}{1 - C \cdot \ln\left(\frac{B(T) + p}{B(T) + p_{ref}}\right)} \quad (3)$$

where $\rho(T, p_{ref})$ is the density as a function of temperature at a reference pressure, given by the following equation:

$$\rho(T, p_{ref}) = \sum_{i=0}^m A_i T^i \quad (4)$$

The reference pressures (p_{ref}) used in this work are provided in Table 6.

C is a temperature and pressure independent parameter and $B(T)$ is a temperature dependent parameter given by:

$$B(T) = \sum_{j=0}^n B_j T^j \quad (5)$$

Table 6 gathers the fitting parameters of Equation 3 obtained for each of the ternary and multicomponent systems of this work. The absolute average deviation as well as the standard deviations of the fit, σ for Equation 4 and σ^* for Equation 3 are also presented in Table 6.

Table 6. Parameters obtained for the modified Tammann-Tait (Equation 3) fit of experimental data. σ is the standard deviations of the fit for Equation 4 and σ^* for Equation 3.

	C ₁ -C ₄ -C ₁₀	C ₁ -C ₄ -C ₁₂	Low GOR	High GOR
p_{ref} / MPa	40	40	40	60
A_0 / g·cm ⁻³	0.852	1.3261	0.956	0.5571
$10^4 \cdot A_1$ / g·cm ⁻³ ·K ⁻¹	-18.67	-57.167	-15.32	3.943
$10^7 \cdot A_2$ / g·cm ⁻³ ·K ⁻²	13.3	111.44	8.9	-38.24
$10^9 \cdot A_3$ / g·cm ⁻³ ·K ⁻³	—	-8.01	—	4.07
$10^3 \cdot \sigma$ / g·cm ⁻³	0.3	0.6	0.7	0.3
C	0.128	0.138	0.11	0.1372
B_0 / MPa	123.9	88.3	261.2	135.0
B_1 / MPa·K ⁻¹	-0.6756	-0.514	-1.178	-0.713
$10^3 \cdot B_2$ / MPa·K ⁻²	0.724	0.544	1.205	0.700
$10^3 \cdot \sigma^*$ / g·cm ⁻³	3.1	2.5	1.0	0.8
AAD / %	0.5	0.4	0.1	0.1

The predictive capability of density through the different models is depicted in Figure 2 where experimental density data has been plotted along with model predictions as a function of pressure at selected temperatures. It can be easily observed that PC-SAFT is the model that predicts more accurately the experimental density data measured in the present work. In order to have a quantitative comparison of the performance of the different models we present in Figure 3 the absolute average deviation found for every model. It can be observed that the best density predictions are obtained through PC-SAFT, which has an overall AAD lower than 1.0%. The other models analyzed, i.e., SRK, PR and SBWR provide a poorer performance, being the worst predictive results obtained with SRK (average AAD of 8.5%). The average AAD obtained for PR and SBWR were 3.8% and 5.1 %, respectively. Thus, it can be stated that PC-SAFT presents the best performance followed by PR, whereas the worst performance is given by SRK. These results are in agreement with a previous study by Yan et al.²⁵, who tested these models for the density prediction of 35 reservoir fluids, finding that PC-SAFT and PR yield the smallest deviations with PC-SAFT being slightly better. They also reported that the worst prediction was obtained through SRK.

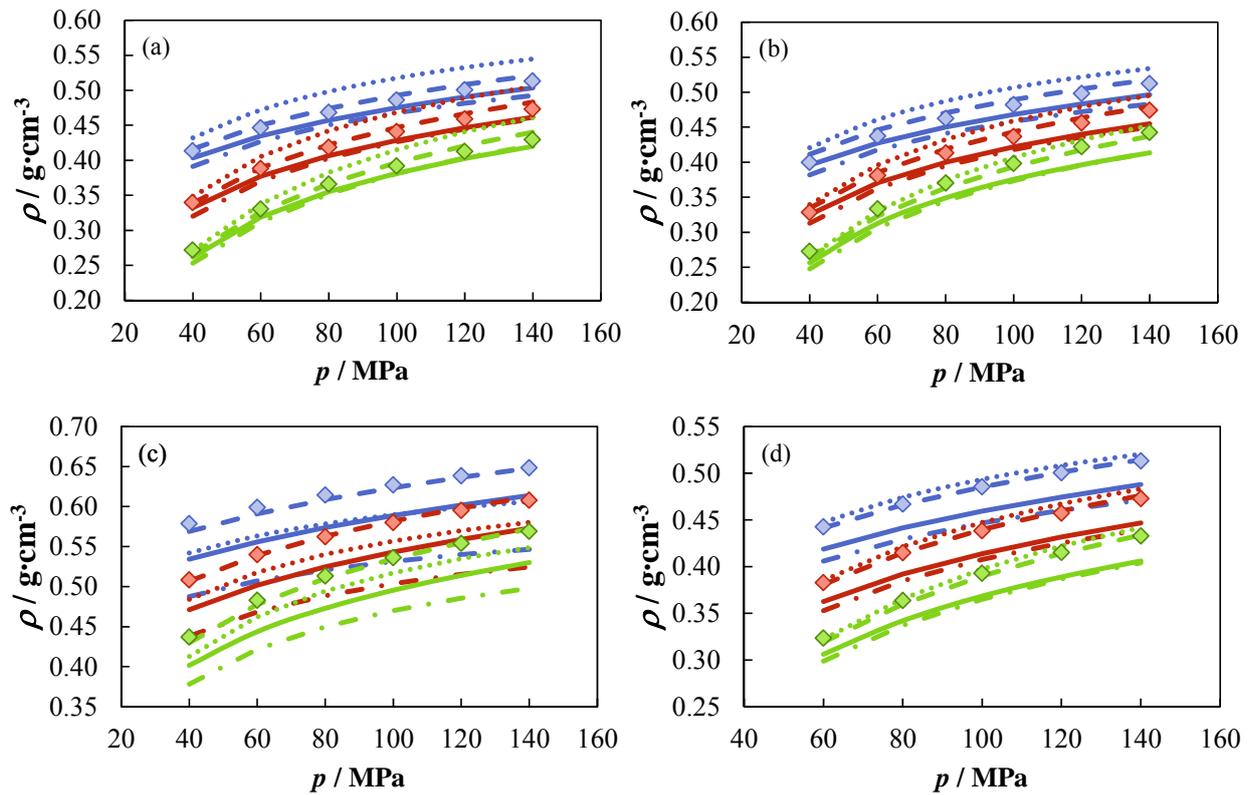


Figure 2. Experimental density values (\blacklozenge) and model predictions at ($\blue\lozenge$) 298.15 K, ($\red\lozenge$) 373.15 K and ($\green\lozenge$) 463.15 K. (a) C1-C4-C10, (b) C1-C4-C12, (c) low GOR and (d) high GOR mixtures. ($- \bullet -$) SRK, (\dots) PR, ($- -$) PC-SAFT, ($-$) SBWR.

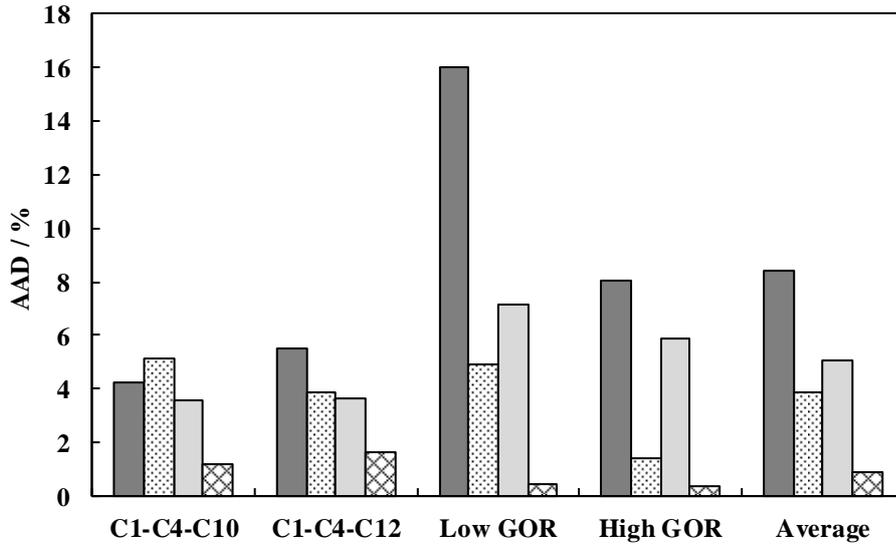


Figure 3. Absolute average deviation (AAD) obtained in the prediction of the experimental density values measured in this work. SRK (■), PR (▨), SBWR (■) and PC-SAFT (▩).

3.2. Isothermal compressibility

The isothermal compressibility values (κ_T) were obtained through differentiation from the modified Tammann-Tait fitting of the experimental density values according to the following equation:

$$\kappa_T(T, p) = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (6)$$

Thus, $\kappa_T(T, p)$ can be written as follows:

$$\kappa_T(T, p) = \frac{C}{(B(T) + p) \left(1 - C \ln \frac{B(T) + p}{B(T) + p_{ref}} \right)} \quad (7)$$

The obtained isothermal compressibility values are summarized in Table 7. The expected trend of this property with temperature and pressure was found, that is, it increases with temperature along isobars and it decreases with pressure along isotherms. The κ_T values are also plotted in Figure 4 at selected temperatures as a function of pressure for the different systems studied, along with model calculations for this property. The system that presents the lower compressibility is, as expected, the low GOR mixture with values ranging from $0.89 \cdot 10^{-3}$ to $3.59 \cdot 10^{-3}$ MPa⁻¹ under the studied experimental conditions. The gas mixtures C1-C4-C10, C1-C4-C12 and high GOR present similar compressibility values which differ in average $0.22 \cdot 10^{-3}$ MPa⁻¹ when compared under the same temperature and pressure conditions.

Table 7. Isothermal compressibility values^a, $10^3 \kappa_T$ (MPa⁻¹), of the ternary and multicomponent alkane mixtures at temperature T and pressure p .

T/K	p/MPa			
	60.0	80.0	100.0	120.0
C ₁ -C ₄ -C ₁₀				
278.15	2.62	1.98	1.61	1.36
298.15	2.94	2.17	1.73	1.46
323.15	3.40	2.42	1.90	1.58
348.15	3.91	2.69	2.08	1.72
373.15	4.47	2.98	2.27	1.86
423.15	5.55	3.51	2.63	2.12
463.15	5.97	3.72	2.77	2.23
C ₁ -C ₄ -C ₁₂				
298.15	3.48	2.52	2.01	1.68
323.15	3.93	2.77	2.17	1.80
348.15	4.42	3.03	2.35	1.94
373.15	4.94	3.30	2.53	2.07
423.15	5.90	3.79	2.86	2.33
463.15	6.30	3.99	3.00	2.44
Low GOR				
298.15	1.48	1.20	1.02	0.89
323.15	1.73	1.37	1.14	0.98
348.15	2.02	1.55	1.27	1.08
373.15	2.37	1.75	1.40	1.18
423.15	3.12	2.16	1.67	1.37
463.15	3.59	2.40	1.82	1.48
High GOR				
298.15	—	2.23	1.77	1.48
323.15	—	2.52	1.96	1.61
348.15	—	2.84	2.15	1.75
373.15	—	3.19	2.36	1.89
423.15	—	3.92	2.76	2.16
463.15	—	4.41	3.02	2.34

^aRelative expanded isothermal compressibility uncertainty $U_r(\kappa_T)$ ($k=2$): 0.01

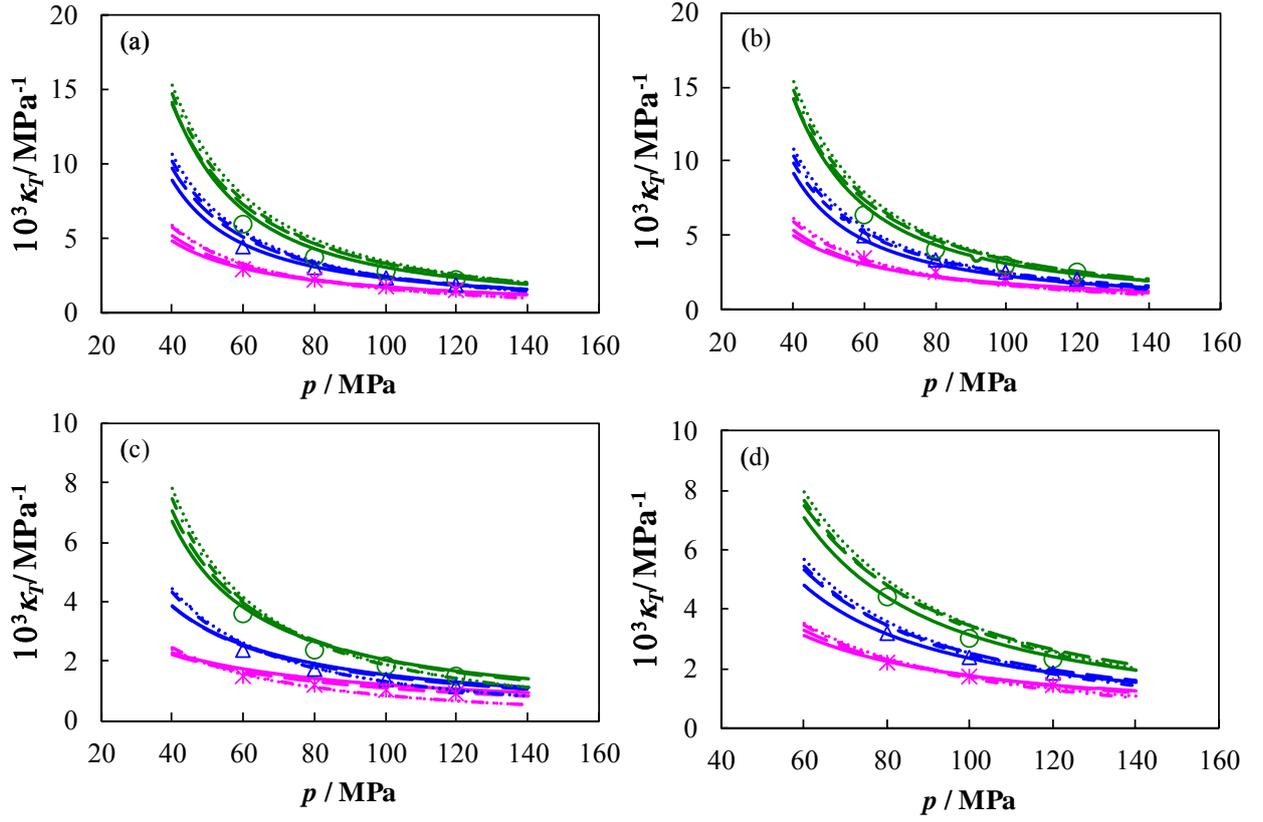


Figure 4. Isothermal compressibility, κ_T , of the ternary and multicomponent mixtures measured in this work as a function of pressure at ($*$) 298.15 K, (Δ) 373.15 K and (\circ) 463.15 K. (a) C₁-C₄-C₁₀, (b) C₁-C₄-C₁₂, (c) low GOR and (d) high GOR mixtures. (— • —) SRK, (•••) PR, (— —) PC-SAFT, (—) SBWR.

3.3. Excess volume

Excess volumes (V^E) of the analyzed mixtures were obtained through the following equation:

$$V^E(T, p) = \frac{\sum_{i=1}^n (x_i M_i)}{\rho_{mix}(T, p)} - \sum_{i=1}^n \left(x_i \frac{M_i}{\rho_i(T, p)} \right) \quad (8)$$

where n is the number of compounds in the mixture, ρ_{mix} is the measured density of the mixture, and x_i , M_i and ρ_i are the mole fraction, the molecular weight and the density of the i th compound in the mixture, respectively.

In order to obtain the values of the excess volumes through equation (8), density data of the pure compounds at the different temperatures and pressures are required. These values were taken from literature, and the literature sources are summarized in Table 8.

Table 8. References for the density data of the pure compounds used in Equation (8) in different temperature (T) and pressure (p) ranges.

Compound	T /K	p / MPa	Density reference
methane	(278 to 463)	(40 to 140)	Setzmann and Wagner ²⁹ REFPROP ³⁰
n-butane	(278 to 463)	(40 to 140)	Bücker and Wagner ³¹ REFPROP ³⁰
n-octane	(373 to 463)	(40 to 140)	Span and Wagner ³² REFPROP ³⁰
n-decane	(278 to 463)	(40 to 140)	Regueira et al. ²⁰
n-dodecane	(373 to 463)	(40 to 140)	Lemmon and Huber ³³ REFPROP ³⁰
n-hexadecane	(373 to 463)	(40 to 60)	Regueira et al. ³⁴
	373	(80 to 140)	Dymond et al. ^{35,*}
	(423 to 463)	(80 to 140)	Wu et al. ^{36,*}
n-eicosane	(373 to 463)	(40 to 140)	Doolittle ^{37,*}

*A correlation and interpolation of the reported density data has been performed in the present work.

*Data interpolation was performed by using the modified Tait Equation provided in the reference.

The excess volumes obtained for the studied systems are presented in Table 9. All the V^E values were found to be negative. This fact can be explained by the packing of molecules of different sizes. The excess volume becomes more negative as the pressure decreases and the temperature increases. These trends of the excess volume with temperature and pressure were previously observed in the study of other alkane mixtures,^{20, 34} n-hexane/n-decane, n-hexane/n-hexadecane and methane/n-decane. The excess volumes determined in this work are plotted in Figure 5 for the systems studied in this work. It is worthwhile to note the large negative value of this property found at the lowest pressures and highest temperatures studied, which can be explained by the presence of supercritical compounds in the mixture. Under the experimental pressure and temperature conditions presented in Table 9 all the pure compounds are liquids except for n-butane at 463.15 K and methane in the whole p , T range, which are in supercritical state. Ott et al.³⁸ have previously explained, based on the study of the binary system propane/ethane, that a large negative contribution to V^E can result from the condensation of supercritical ethane into liquid propane. The magnitude of the condensation term will depend on the extent of gas-like behaviour of the supercritical fluid. The contribution of this phenomenon being more important when the supercritical fluid has a larger gas-like behaviour, that is when pressure decreases and temperature increases.

Table 9. Excess volume^a, V^E , of the ternary and multicomponent alkane mixtures in $\text{cm}^3\text{mol}^{-1}$ at temperature T and pressure p .

T /K	p /MPa					
	40.0	60.0	80.0	100.0	120.0	140.0
C ₁ -C ₄ -C ₁₀						

278.15	-5.68	-2.90	-1.72	-1.15	-0.84	-0.62
298.15	-6.61	-3.29	-1.93	-1.27	-0.90	-0.64
323.15	-7.71	-3.82	-2.25	-1.48	-1.06	-0.75
348.15	-8.71	-4.38	-2.63	-1.75	-1.26	-0.87
373.15	-9.55	-4.94	-3.02	-2.01	-1.42	-0.94
423.15	-10.80	-6.06	-3.73	-2.42	-1.60	-0.89
463.15	-11.09	-6.58	-3.94	-2.46	-1.64	-0.98
C ₁ -C ₄ -C ₁₂						
298.15	-5.34	-2.70	-1.71	-1.26	-1.03	-0.90
323.15	-6.08	-2.98	-1.82	-1.35	-1.12	-0.98
348.15	-6.86	-3.43	-2.09	-1.49	-1.22	-1.07
373.15	-8.34	-4.52	-2.86	-1.95	-1.54	-1.49
423.15	-11.39	-7.01	-4.51	-3.20	-2.73	-2.56
463.15	-13.60	-8.73	-5.75	-4.28	-3.73	-3.43
Low GOR						
373.15	-16.23	-8.49	-5.45	-3.93	-3.04	-2.46
423.15	-19.45	-10.41	-6.78	-4.94	-3.82	-3.09
463.15	-21.74	-12.09	-8.00	-5.87	-4.54	-3.61
High GOR						
373.15	—	-6.05	-3.91	-2.84	-2.20	-1.77
423.15	—	-6.88	-4.66	-3.47	-2.71	-2.15
463.15	—	-7.58	-5.39	-4.11	-3.22	-2.55

^aExpanded uncertainty of the excess volume $U(V^E)$ ($k=2$): 0.4 – 2.7 cm³mol⁻¹

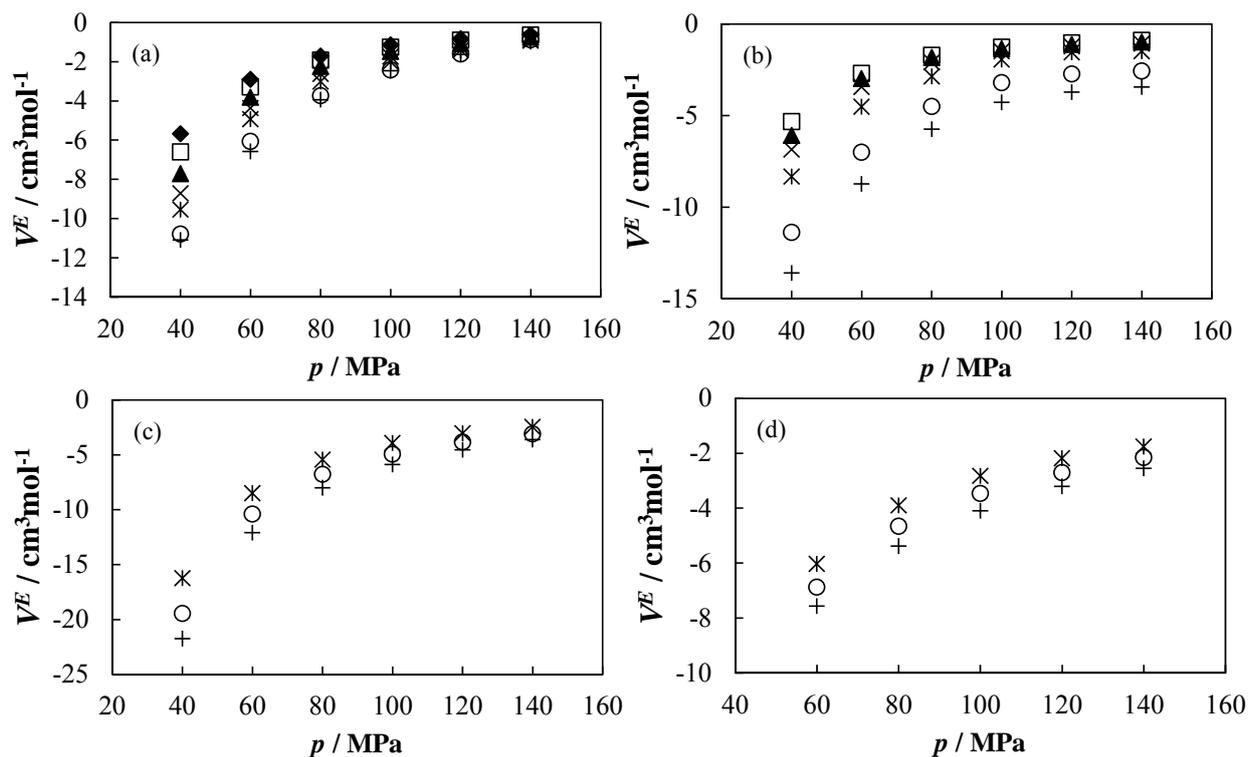


Figure 5. Excess volume, V^E , of the ternary and multicomponent mixtures measured in this work as a function of pressure. (a) C₁-C₄-C₁₀, (b) C₁-C₄-C₁₂, (c) low GOR and (d) high GOR mixtures. (◆) 278.15 K, (□) 298.15 K, (▲) 323.15 K, (×) 348.15 K, (*) 373.15 K, (○) 423.15 K and (+) 463.15 K.

Figure 6 depicts the prediction of the excess volume of the studied systems along with experimental data at selected temperatures. It can be observed that all the analyzed models under predict the magnitude of the excess volume, especially at high temperatures. It is interesting to note that SBWR gives the poorest prediction of this property, whereas the predictions through SRK, PR and PC-SAFT are very similar. In general the models give a good representation of the dependence of the excess volume with pressure but they under predict the dependence with temperature.

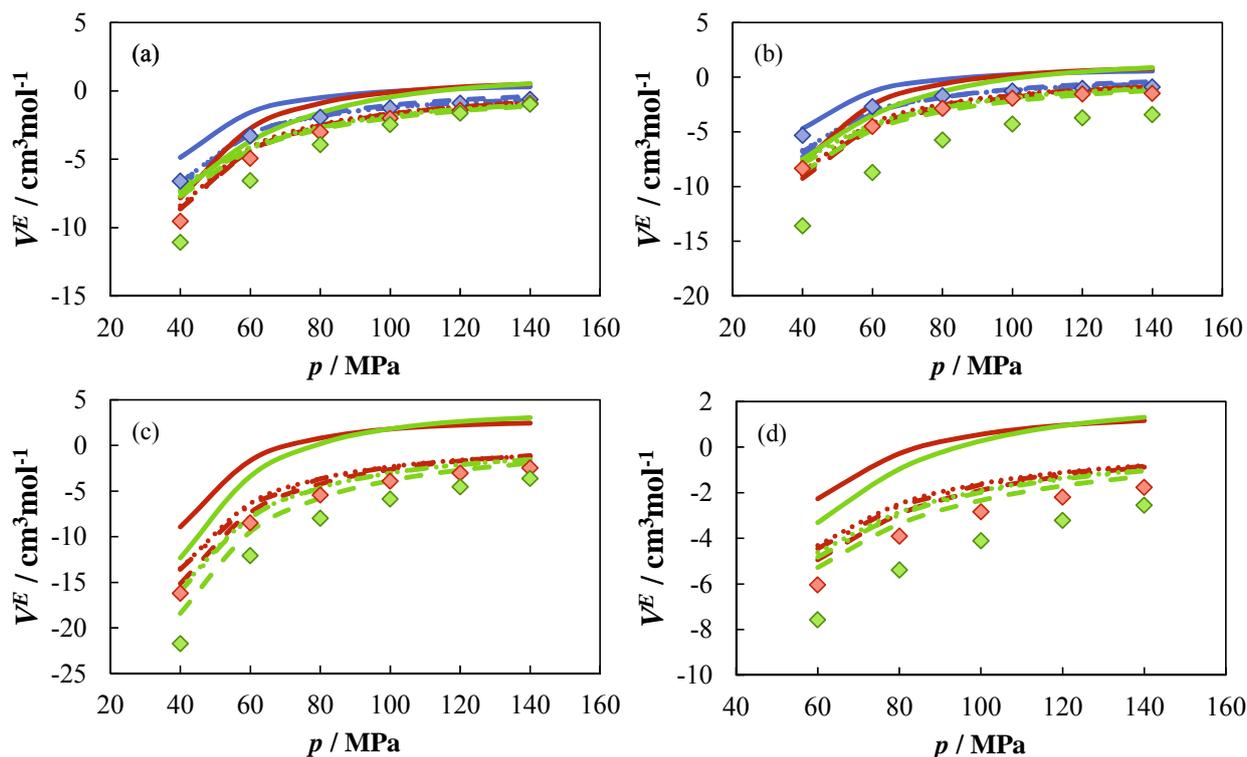


Figure 6. Experimental values of the excess volume (\blacklozenge) and model predictions at (\blacklozenge) 298.15 K, (\blacklozenge) 373.15 K and (\blacklozenge) 463.15 K. (a) C₁-C₄-C₁₀, (b) C₁-C₄-C₁₂, (c) low GOR and (d) high GOR mixtures. (—•—) SRK, (•••) PR, (---) PC-SAFT, (—) SBWR.

4. Conclusions

New experimental density data of four ternary and multicomponent mixtures prepared as models for reservoir fluids have been provided in broad temperature and pressure ranges. The highest density values were those of the liquid low GOR system, whereas those of the gas systems (C₁-C₄-C₁₀, C₁-C₄-C₁₂ and high GOR) are very similar showing a maximum AAD of 1.4% when the density of two systems is compared. The isothermal compressibility values of the studied gas systems are also very similar showing an average difference of $0.22 \cdot 10^{-3} \text{ MPa}^{-1}$. The excess volumes determined in this work are negative and they become more negative when the pressure decreases and the temperature increases. The absolute values of this property have been found to be relatively high at the lowest pressures and highest temperatures studied, which can be explained by the presence of supercritical compounds in the mixture.

The best prediction of the experimental density data was obtained through PC-SAFT, followed by PR, whereas the worst density prediction was obtained with SRK. Despite this difference in the density prediction, it has been found that these three models provide similar prediction of the excess volume of the studied systems. The three of them under predict the magnitude of the excess volume.

This fact indicates that work is still needed to improve the predictive performance of the studied models regarding excess volume.

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