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Volumetric Properties for the Binary Systems Hexane + Octane and Hexane + Decane at High Temperatures and Pressures

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ABSTRACT: Volumetric properties (p, ρ, T, x_1) of two binary linear alkane systems are reported in the temperature range of (313 to 363) K and up to 25 MPa. Binary mixtures were prepared at compositions of (x_1 = 0.1654, 0.2199, 0.5749, 0.7995, and 0.9308) for hexane (1) + octane (2) and hexane (1) + decane (2) at (x_1 = 0.0456, 0.2185, 0.4968, 0.7524, and 0.8991) in mole fraction. Experimental densities were measured in a vibrating-tube densimeter, DMA HPM from Anton Paar, using water and nitrogen as reference fluids. The excess molar volumes, isobaric thermal expansivities, and isothermal compressibilities for these systems were computed from experimental data using a six-parameter modified Toscani and Szwarc equation.

INTRODUCTION

Linear alkane mixtures have applications in chemical and petroleum industries. Volumetric properties and phase behavior of the binary alkane mixtures as a function of temperature, pressure, and composition is essential for the development of thermodynamic models such as equations of state and new possible processes. The p, ρ, T, and x properties of alkane mixtures have been mainly studied at atmospheric pressure and maximum temperatures of 313 K.[1−10] In the case of higher temperatures and above atmospheric pressure, scarce experimental density data are published in a wide range of conditions.[11−20]

Cooper and Asfour[2] and Aucejo et al.[7] obtained the densities for the hexane + decane mixtures at atmospheric pressure using the vibrating-tube densimeter technique. For the same system, Takagi and Teranishi[14] reported density measurements using the ultrasonic speed method at 298.15 K and no more than three pressures, (0.1, 50, and 100) MPa. These publications show the same trend for the density data at similar conditions of pressure, temperature, and composition. Katzenski and Schneider[20] published excess molar volumes for binary linear alkane mixtures between hexane, octane, decane, dodecane, and tetradecane from (10 to 200) MPa and 298.15 K but only at equimolar composition.

In general, all of the above publications report similar density behavior; it increases with pressure increments at fixed temperature and composition, while it decreases when the temperature is increased and also when the mixture is richer in the light component. In the case of the excess molar volumes, these show quite low negative values and are near to zero when the number of carbon atoms of both components is closer.

The purpose of this work is to present the experimental density behavior, calculated excess volumes, and derivative properties of binary alkane mixtures in the compressed liquid region. Densities of the binary hexane + octane and hexane + decane systems were obtained in the whole range of composition from T = (313.15 to 363.15) K and up to 25 MPa.

EXPERIMENTAL SECTION

Apparatus. The schematic diagram of the experimental apparatus employed in this work is shown in Figure 1. This is based on the static−synthetic method and the densimeter technique for the measurement of the volumetric properties. The vibrating-tube densimeter (VTD) Anton Paar DMA HPM was connected through a needle valve to a loading cell. The pressure of the system was increased by using a piston that separates the studied fluid from the pressurizing fluid inside of the cell.

An air bath (France Etuves, XL074SP) was used to control the loading cell temperature, while the VTD temperature was kept constant by a circulating liquid bath (Polyscience, 9510); nevertheless, the densimeter was also located inside the oven. Pressure was measured with a Bourdon-Sedeme transducer (S242) connected to a digital multimeter (HP, 34401A). Two platinum resistance thermometers (PT-100-Ω) were used for the system temperature measurements. Thermometers send the signals to a digital temperature indicator (AΣΛ, F-250). An evaluation unit (mPDS 2000 V3) with a resolution of $1 \cdot 10^{-3}$ μs displayed the vibrating period of the fluid.

To observe directly the system behavior, the multimeter, temperature indicator, and evaluation unit were communicated with the computer through a multiparallel RS-232/USB serial interface adapter (model: 2403, Sealevel).

Density Measurements. The experimental methodology for the density measurements consisted basically of the following.

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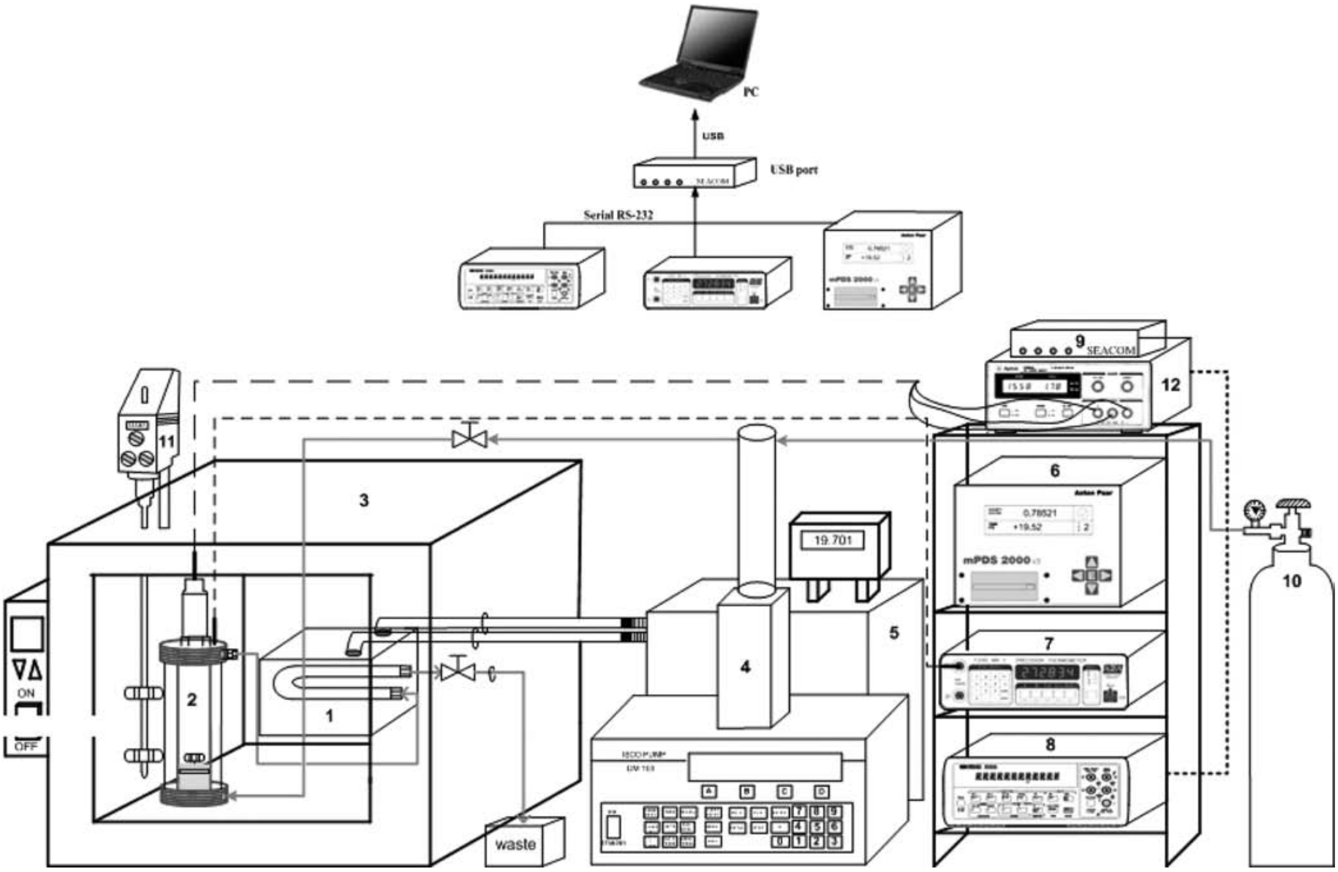

Figure 1. Experimental apparatus with data acquisition configuration: 1, vibrating tube densimeter; 2, loading cell; 3, oven; 4, syringe pump; 5, circulating liquid bath; 6, evaluation unit; 7, temperature indicator; 8, multimeter; 9, serial interface adapter; 10, nitrogen cylinder; 11, stirring device; 12, power supply.

Table 1. Chemicals Used in This Work

	CAS	supplier	certified purity	water content
			mole fraction	mole fraction
hexane	[110-54-3]	Sigma-Aldrich	0.995	$1.7 \cdot 10^{-4}$
octane	[111-65-9]	Sigma-Aldrich	0.995	$1.8 \cdot 10^{-4}$
decane	[124-18-5]	Sigma-Aldrich	0.997	$2.8 \cdot 10^{-4}$
water	[7732-18-5]	Sigma-Aldrich	0.9995	ND[a]
nitrogen	[7727-37-9]	Air Products-Infra	0.99998	ND

[a] ND: not determined.

Calibration of thermometers was performed using a resistance thermometry bridge (AΣΛ, F-350). The pressure transducer was calibrated against a dead weight balance (DH Instruments, 5304). VTD calibration[21] was carried out using water and nitrogen as reference fluids. Then, densities of each mixture were computed with the following equation:

$$\rho_M(p, T, \tau) = \rho_{H_2O}(p, T) + \frac{[\tau_M^2(p, T) - \tau_{H_2O}^2(p, T)][\rho_{H_2O}(p, T) - \rho_{N_2}(p, T)]}{\tau_{H_2O}^2(p, T) - \tau_{N_2}^2(p, T)} \quad (1)$$

where ρ_M is the density of the mixture while ρ_{H_2O} and ρ_{N_2} represent the densities of water and nitrogen, respectively. Water density was calculated using the Wagner and Pruss[22] equation of state, while the corresponding density for nitrogen was the proposed by Span et al.[23] The vibrating period of the mixture is represented as τ_M.

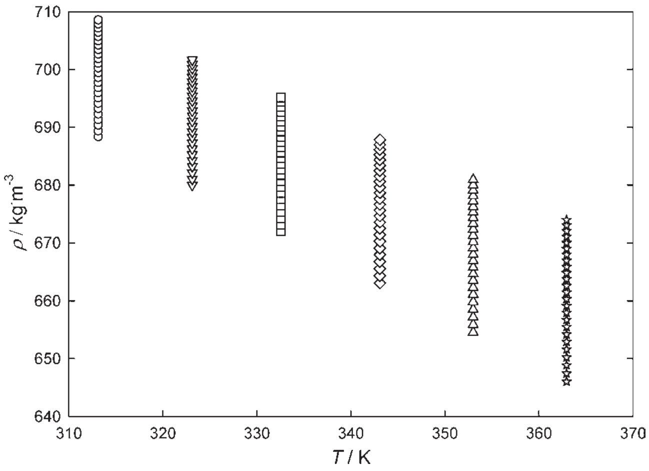

Figure 2. Density behavior with respect to temperature changes for the hexane + decane system at $x_1 = 0.4968$: ○, 313.21 K; ▽, 323.14 K; □, 332.58 K; ◇, 343.08 K; △, 353.01 K; ☆, 362.93 K.

The mixture composition was prepared by means of successive weightings[24] using a comparator balance (Sartorius, MCA 1200)

Table 2. Experimental Densities for the Binary Mixture Hexane (1) + Octane (2) at $x_1 = 0.1654^a$

p	$\rho/\mathrm{kg \cdot m^{-3}}$					
MPa	313.14 K	323.08 K	333.02 K	342.99 K	352.91 K	362.88 K
1.00	682.20	674.04	665.79	657.36	648.87	640.20
2.00	683.10	675.02	666.85	658.52	650.15	641.61
3.00	684.01	676.00	667.91	659.68	651.43	642.98
4.00	684.90	676.97	668.97	660.84	652.68	644.35
5.00	685.84	677.97	670.04	662.01	653.95	645.69
6.00	686.80	678.97	671.11	663.15	655.19	647.04
7.00	687.71	679.95	672.17	664.27	656.40	648.35
8.00	688.62	680.93	673.21	665.40	657.60	649.64
9.00	689.54	681.93	674.28	666.53	658.80	650.92
10.00	690.46	682.90	675.32	667.62	659.99	652.16
11.00	691.38	683.88	676.36	668.73	661.15	653.43
12.00	692.28	684.84	677.38	669.80	662.28	654.65
13.00	693.17	685.79	678.38	670.86	663.41	655.84
14.00	694.06	686.73	679.38	671.91	664.53	657.01
15.00	694.94	687.65	680.34	672.94	665.63	658.17
16.00	695.81	688.56	681.29	673.96	666.68	659.30
17.00	696.65	689.44	682.26	674.95	667.73	660.41
18.00	697.47	690.32	683.15	675.92	668.76	661.50
19.00	698.27	691.15	684.04	676.86	669.76	662.58
20.00	699.05	691.98	684.93	677.79	670.78	663.60
21.00	699.81	692.79	685.79	678.70	671.71	664.63
22.00	700.55	693.57	686.62	679.59	672.65	665.63
23.00	701.28	694.36	687.45	680.47	673.59	666.61
24.00	701.98	695.11	688.25	681.32	674.50	667.57
25.00	702.70	695.85	689.01	682.14	675.39	668.52

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}$ mol·mol^{-1}, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095$ kg·m^{-3}, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2$ kg·m^{-3} with a 0.95 level of confidence ($k \approx 2$).

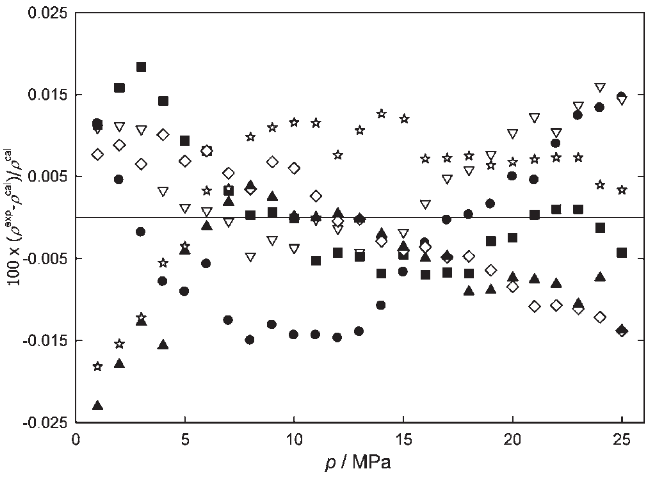

Figure 3. Deviation of experimental density with relation to the calculated data with the six-parameter equation for the hexane + decane system at $x_1 = 0.7524$: ●, 313.18 K; ▽, 323.16 K; ■, 333.10 K; ◇, 343.06 K; ▲, 352.99 K; ☆, 362.93 K.

for each binary alkane mixture. The estimated uncertainty was ± $1 \cdot 10^{-4}$ in mole fraction.

Table 3. Experimental Densities for the Binary Mixture Hexane (1) + Octane (2) at $x_1 = 0.2199^a$

p	$\rho/\mathrm{kg \cdot m^{-3}}$					
MPa	312.91 K	323.07 K	333.04 K	342.94 K	352.85 K	362.88 K
1.00	680.43	672.17	663.81	655.33	646.75	637.97
2.00	681.31	673.14	664.87	656.52	648.04	639.42
3.00	682.24	674.14	665.96	657.67	649.32	640.79
4.00	683.15	675.13	667.04	658.87	650.60	642.17
5.00	684.07	676.14	668.13	660.02	651.87	643.54
6.00	684.99	677.12	669.19	661.18	653.11	644.88
7.00	685.92	678.12	670.26	662.34	654.35	646.21
8.00	686.87	679.13	671.36	663.49	655.57	647.53
9.00	687.80	680.12	672.39	664.60	656.79	648.82
10.00	688.73	681.12	673.44	665.73	657.97	650.09
11.00	689.64	682.09	674.49	666.84	659.16	651.35
12.00	690.55	683.06	675.50	667.93	660.32	652.59
13.00	691.47	684.02	676.53	669.01	661.45	653.81
14.00	692.36	684.97	677.53	670.06	662.57	654.99
15.00	693.23	685.89	678.51	671.09	663.67	656.16
16.00	694.09	686.79	679.46	672.10	664.74	657.29
17.00	694.93	687.68	680.40	673.10	665.80	658.42
18.00	695.75	688.54	681.32	674.07	666.83	659.52
19.00	696.54	689.38	682.23	675.02	667.85	660.60
20.00	697.32	690.21	683.09	675.95	668.84	661.65
21.00	698.10	691.03	683.96	676.87	669.80	662.67
22.00	698.86	691.83	684.80	677.76	670.75	663.67
23.00	699.56	692.58	685.61	678.64	671.68	664.66
24.00	700.29	693.35	686.43	679.49	672.59	665.61
25.00	700.96	694.10	687.22	680.34	673.48	666.56

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}$ mol·mol^{-1}, $u(T) = 0.03$ K, $u(P) = 0.02$ MPa, $u(\rho) = 0.095$ kg·m^{-3}, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2$ kg·m^{-3} with a 0.95 level of confidence ($k \approx 2$).

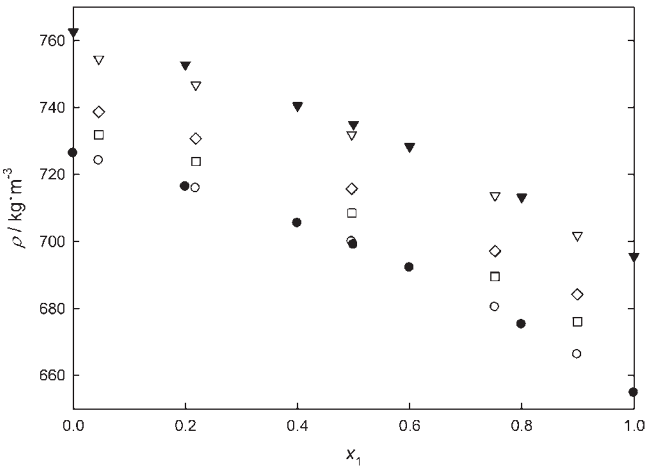

Figure 4. Densities for the hexane (1) + decane (2) system at 298.15 K: ○, ●, 0.1 MPa; □, 10 MPa; ◇, 20 MPa; ▽,▼, 50 MPa. Open and black symbols refer to this work and Takagi and Teranishi,[14] respectively.

The loading cell was placed inside the oven to check for leaks. Then all of the circuits except the cell were degassed. Afterward,

Table 4. Experimental Densities for the Binary Mixture Hexane (1) + Octane (2) at $x_1 = 0.5749$[a]

p	$\rho/\mathrm{kg \cdot m^{-3}}$					
MPa	313.14 K	323.06 K	332.95 K	342.93 K	352.79 K	362.76 K
1.00	666.90	658.22	649.41	640.49	631.40	622.07
2.00	667.85	659.25	650.55	641.81	632.83	623.63
3.00	668.75	660.31	651.69	643.05	634.20	625.20
4.00	669.74	661.34	652.87	644.29	635.57	626.68
5.00	670.74	662.42	654.06	645.58	636.95	628.17
6.00	671.71	663.46	655.21	646.83	638.30	629.67
7.00	672.72	664.53	656.35	648.05	639.63	631.09
8.00	673.69	665.61	657.49	649.28	640.97	632.53
9.00	674.66	666.67	658.63	650.49	642.26	633.92
10.00	675.65	667.73	659.75	651.67	643.53	635.27
11.00	676.63	668.78	660.86	652.87	644.82	636.64
12.00	677.60	669.81	661.96	654.03	646.04	637.96
13.00	678.56	670.83	663.04	655.19	647.27	639.28
14.00	679.50	671.84	664.10	656.31	648.46	640.55
15.00	680.41	672.81	665.14	657.42	649.66	641.82
16.00	681.32	673.78	666.16	658.50	650.79	643.03
17.00	682.20	674.72	667.18	659.57	651.95	644.23
18.00	683.06	675.63	668.14	660.60	653.02	645.42
19.00	683.89	676.52	669.09	661.62	654.11	646.56
20.00	684.72	677.38	670.02	662.60	655.18	647.68
21.00	685.52	678.25	670.93	663.59	656.24	648.78
22.00	686.32	679.10	671.82	664.52	657.22	649.86
23.00	687.10	679.90	672.70	665.48	658.23	650.91
24.00	687.85	680.71	673.55	666.39	659.22	651.95
25.00	688.59	681.47	674.35	667.28	660.15	652.96

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}\ \mathrm{mol \cdot mol^{-1}}$, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095\ \mathrm{kg \cdot m^{-3}}$, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2\ \mathrm{kg \cdot m^{-3}}$ with a 0.95 level of confidence ($k \approx 2$).

Table 5. Experimental Densities for the Binary Mixture Hexane (1) + Octane (2) at $x_1 = 0.7995$[a]

p	$\rho/\mathrm{kg \cdot m^{-3}}$					
MPa	313.14 K	323.10 K	333.02 K	343.00 K	352.92 K	362.90 K
1.00	655.29	646.30	637.16	627.89	618.46	608.76
2.00	656.27	647.41	638.39	629.27	619.98	610.47
3.00	657.26	648.55	639.63	630.64	621.51	612.13
4.00	658.29	649.72	640.91	632.01	623.00	613.77
5.00	659.31	650.83	642.14	633.35	624.48	615.41
6.00	660.34	651.95	643.37	634.69	625.93	616.94
7.00	661.38	653.08	644.60	636.02	627.37	618.50
8.00	662.44	654.18	645.81	637.32	628.79	620.01
9.00	663.49	655.30	647.01	638.61	630.18	621.50
10.00	664.53	656.41	648.19	639.87	631.54	622.96
11.00	665.56	657.51	649.36	641.10	632.86	624.39
12.00	666.56	658.59	650.50	642.32	634.17	625.81
13.00	667.56	659.66	651.63	643.52	635.46	627.18
14.00	668.54	660.72	652.74	644.70	636.72	628.53
15.00	669.51	661.75	653.84	645.87	637.96	629.85
16.00	670.45	662.76	654.91	647.01	639.16	631.14
17.00	671.40	663.74	655.95	648.12	640.35	632.42
18.00	672.32	664.69	656.97	649.21	641.51	633.67
19.00	673.21	665.64	657.98	650.28	642.64	634.88
20.00	674.07	666.56	658.95	651.33	643.75	636.08
21.00	674.92	667.44	659.91	652.33	644.82	637.22
22.00	675.74	668.32	660.83	653.33	645.88	638.34
23.00	676.52	669.16	661.72	654.30	646.92	639.44
24.00	677.27	669.96	662.60	655.24	647.94	640.51
25.00	677.99	670.76	663.44	656.16	648.91	641.57

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}\ \mathrm{mol \cdot mol^{-1}}$, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095\ \mathrm{kg \cdot m^{-3}}$, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2\ \mathrm{kg \cdot m^{-3}}$ with a 0.95 level of confidence ($k \approx 2$).

the stirring device was turned on to mix the sample, and the system temperature was fixed to the first experimental temperature (~313 K). The data acquisition software was turned on to register the data.

Density measurements started until pressure and temperature were stable. It was considered when values of the three variables (T, p, τ) changed within the uncertainty of each instrument. Then the experimentation began at the lowest pressure (1 MPa), after the stabilization of the system, T, p, and vibrating period of the mixture τ_M were registered. The pressure was increased for each 1 MPa, and these variables were again registered based on the same criteria. This procedure was repeated up to reach the maximum pressure of 25 MPa. The oven and liquid bath temperatures were then adjusted with an increment of 10 K, and the same procedure was followed until to reach the maximum temperature (~363 K).

Uncertainties of all variables were calculated following a National Institute of Standards and Technology (NIST) publication.[25] Uncertainties were ± 0.03 K for temperature and ± 0.02 MPa for pressure, while the density was within 0.2 $\mathrm{kg \cdot m^{-3}}$.

Materials. Hydrocarbons and water were purchased from Sigma-Aldrich. Infra Air Products supplied the nitrogen. The water content for alkanes was determined using a Karl Fischer coulometer (Metrohm, 831). Chemicals were used as received without any further purification. Certified purities and water content of the compounds are given in Table 1.

RESULTS AND DISCUSSION

Densities for linear alkane mixtures were obtained isothermally from (313 to 363) K in temperature intervals of 10 K and pressures up to 25 MPa. The experimental results for the hexane (1) + octane (2) and the hexane (1) + decane (2) mixtures are listed in Tables 2 to 11 for different compositions. The behavior of this property varies inversely with respect to temperature increases; it increases when the other decreases. In contrast, this property is proportional to pressure changes as shown in Figure 2.

The experimental densities were correlated with a six-parameter correlation, which is a modification of the empirical expression of Toscani and Szwarc (TS).[26] This modified empirical equation is expressed as

$$\rho_M = \frac{d_3 - d_4 T + d_5 T^{1/2} + d_6 p}{d_1 + d_2 p} \tag{2}$$

The optimized parameters are listed in Table 12 for each mixture. An example of the deviation between the experimental data and the correlated results is depicted in Figure 3 for the hexane + decane mixture at $x_1 = 0.7524$. The maximum deviation reported

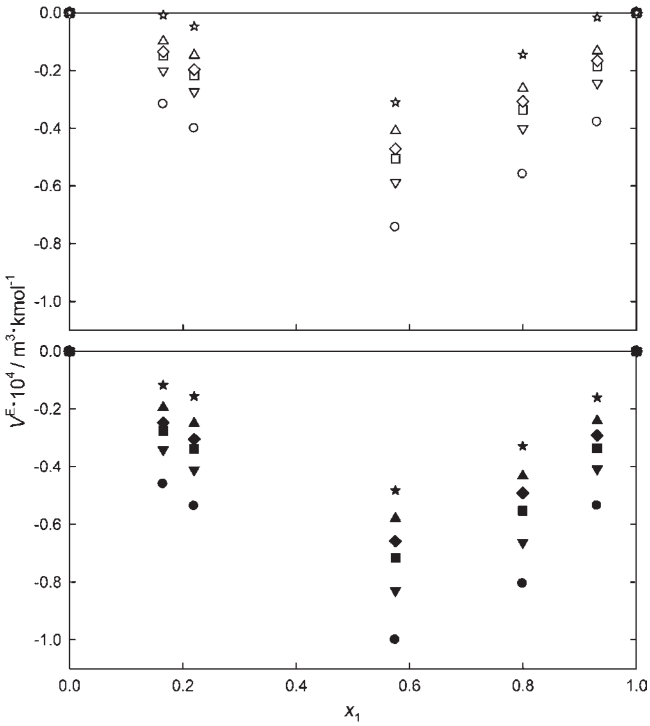

Figure 5. Excess molar volumes for the hexane (1) + octane (2) system at: ○, ●, 1 MPa; ▽, ▼, 5 MPa; □, ■, 10 MPa; ◇, ◆, 15 MPa; △, ▲, 20 MPa; ☆, ★, 25 MPa. Open and black symbols denote ~313 K and ~363 K, respectively.

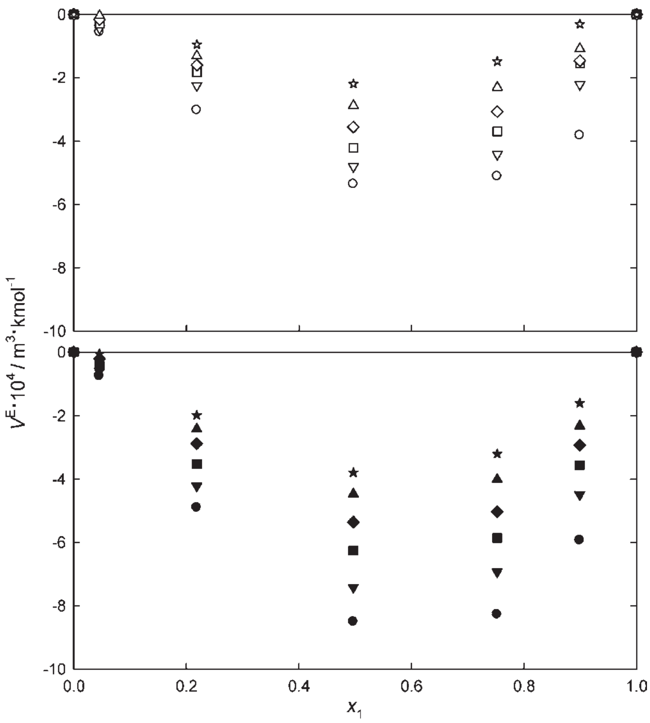

Figure 6. Behavior of the excess molar volume with the temperature and pressure for the hexane (1) + decane (2) system at: ○, ●, 1 MPa; ▽, ▼, 5 MPa; □, ■, 10 MPa; ◇, ◆, 15 MPa; △, ▲, 20 MPa; ☆, ★, 25 MPa. Open and black symbols denote ~313 K and ~363 K, respectively.

Table 6. Experimental Densities for the Binary Mixture Hexane (1) + Octane (2) at x_1 = 0.9308[a]

p	ρ/kg·m^{-3}					
MPa	313.14 K	323.09 K	333.01 K	342.98 K	352.91 K	362.89 K
1.00	647.60	638.41	629.03	619.48	609.77	599.76
2.00	648.65	639.57	630.32	620.92	611.36	601.55
3.00	649.73	640.76	631.62	622.34	612.95	603.31
4.00	650.78	641.92	632.91	623.76	614.51	605.04
5.00	651.85	643.10	634.20	625.17	616.06	606.72
6.00	652.92	644.29	635.48	626.56	617.57	608.38
7.00	654.00	645.46	636.74	627.93	619.06	610.01
8.00	655.08	646.63	638.01	629.29	620.53	611.58
9.00	656.16	647.79	639.26	630.63	621.96	613.16
10.00	657.23	648.93	640.48	631.94	623.39	614.68
11.00	658.29	650.05	641.70	633.24	624.78	616.17
12.00	659.33	651.17	642.89	634.53	626.15	617.64
13.00	660.36	652.26	644.06	635.77	627.49	619.07
14.00	661.38	653.35	645.22	637.01	628.80	620.48
15.00	662.38	654.41	646.35	638.23	630.08	621.85
16.00	663.36	655.45	647.46	639.42	631.35	623.20
17.00	664.33	656.47	648.54	640.57	632.57	624.51
18.00	665.28	657.47	649.61	641.70	633.78	625.80
19.00	666.20	658.44	650.63	642.81	634.96	627.06
20.00	667.10	659.39	651.64	643.91	636.11	628.28
21.00	667.97	660.32	652.62	644.95	637.22	629.48
22.00	668.80	661.20	653.55	645.97	638.32	630.64
23.00	669.60	662.07	654.50	646.98	639.39	631.79
24.00	670.36	662.91	655.39	647.95	640.43	632.90
25.00	671.10	663.72	656.28	648.91	641.44	634.01

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}$ mol·mol^{-1}, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095$ kg·m^{-3}, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2$ kg·m^{-3} with a 0.95 level of confidence ($k \approx 2$).

for this mixture is ± 0.024 %, indicating that the experimental data shows good agreement because they are within the experimental uncertainty. The absolute average deviation (% AAD) for the correlated densities is summarized in Table 12 for each mixture. This modified correlation (MTS) was used to have a better representation of the experimental data compared with the original TS model.[26] Deviations in terms of %AAD for the TS model are two times higher than those obtained with the MTS model for all of the compositions.

Densities for the hexane + decane system were extrapolated at 298.15 K using eq 2 to compare this trend against the densities reported by Takaki and Teranishi[14] at (0.1 and 50) MPa. Our density trend and that from the literature agree with respect to the mixture composition at 0.1 MPa as observed in Figure 4. However, the MTS correlation was unable to perform the extrapolation at 50 MPa. Differences between both sets of data at this pressure are approximately about 5 kg·m^3.

The excess molar volumes V^E were computed from the experimental data. The density of pure components was obtained from the Thermophysics Data Bank available at NIST.[27] The calculation was performed using eq 3.

$$V^E = \frac{x_1 \mathrm{MW}_1 + (1 - x_1)\mathrm{MW}_2}{\rho_M} - \left[\frac{x_1 \mathrm{MW}_1}{\rho_1} + \frac{(1 - x_1)\mathrm{MW}_2}{\rho_2}\right] \qquad (3)$$

Table 7. Experimental Densities for the Binary Mixture Hexane (1) + Decane (2) at x_1 = 0.0456[a]

p	ρ/kg·m^{-3}					
MPa	313.18 K	323.14 K	333.12 K	343.05 K	352.99 K	362.91 K
1.00	713.33	705.56	697.88	690.21	682.21	674.50
2.00	714.22	706.52	698.90	691.25	683.34	675.70
3.00	715.11	707.47	699.91	692.26	684.46	676.88
4.00	715.98	708.40	700.90	693.30	685.57	678.04
5.00	716.84	709.32	701.88	694.32	686.64	679.18
6.00	717.69	710.22	702.84	695.32	687.71	680.32
7.00	718.53	711.11	703.78	696.31	688.77	681.43
8.00	719.34	711.99	704.71	697.29	689.81	682.51
9.00	720.15	712.86	705.63	698.26	690.83	683.59
10.00	720.95	713.72	706.54	699.22	691.84	684.65
11.00	721.74	714.56	707.42	700.16	692.84	685.70
12.00	722.51	715.39	708.30	701.08	693.82	686.71
13.00	723.28	716.21	709.16	702.00	694.79	687.73
14.00	724.03	717.02	710.01	702.89	695.75	688.73
15.00	724.78	717.82	710.86	703.77	696.69	689.71
16.00	725.51	718.60	711.67	704.64	697.62	690.69
17.00	726.24	719.38	712.48	705.50	698.54	691.65
18.00	726.96	720.14	713.29	706.36	699.44	692.61
19.00	727.67	720.90	714.08	707.20	700.33	693.55
20.00	728.36	721.64	714.87	708.02	701.21	694.48
21.00	729.05	722.37	715.64	708.84	702.11	695.43
22.00	729.74	723.10	716.39	709.65	702.98	696.32
23.00	730.42	723.81	717.15	710.45	703.83	697.22
24.00	731.08	724.52	717.89	711.25	704.67	698.09
25.00	731.73	725.21	718.63	712.03	705.49	698.96

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}$ mol·mol^{-1}, $u(T)$ = 0.03 K, $u(p)$ = 0.02 MPa, $u(\rho)$ = 0.095 kg·m^{-3}, and the combined expanded uncertainty U_c is $U_c(\rho)$ = 0.2 kg·m^{-3} with a 0.95 level of confidence ($k \approx 2$).

Table 8. Experimental Densities for the Binary Mixture Hexane (1) + Decane (2) at x_1 = 0.2185[a]

p	ρ/kg·m^{-3}					
MPa	313.17 K	323.14 K	333.08 K	343.06 K	353.00 K	362.95 K
1.00	704.92	697.10	689.16	681.09	673.09	664.98
2.00	705.74	698.02	690.17	682.19	674.25	666.23
3.00	706.66	698.97	691.16	683.33	675.39	667.46
4.00	707.53	699.88	692.16	684.40	676.51	668.71
5.00	708.39	700.82	693.16	685.47	677.65	669.93
6.00	709.25	701.75	694.13	686.52	678.75	671.12
7.00	710.11	702.67	695.10	687.54	679.82	672.27
8.00	710.96	703.58	696.06	688.57	680.92	673.43
9.00	711.80	704.45	697.02	689.57	681.98	674.54
10.00	712.63	705.32	697.94	690.55	683.03	675.66
11.00	713.46	706.19	698.86	691.53	684.07	676.75
12.00	714.27	707.05	699.77	692.48	685.08	677.81
13.00	715.05	707.88	700.66	693.45	686.09	678.85
14.00	715.84	708.71	701.54	694.36	687.09	679.90
15.00	716.63	709.54	702.39	695.27	688.08	680.96
16.00	717.40	710.33	703.25	696.19	689.03	681.94
17.00	718.15	711.14	704.09	697.07	689.97	682.95
18.00	718.88	711.93	704.93	697.94	690.90	683.90
19.00	719.62	712.70	705.76	698.83	691.79	684.89
20.00	720.34	713.47	706.56	699.68	692.70	685.85
21.00	721.06	714.23	707.37	700.53	693.59	686.79
22.00	721.76	714.97	708.17	701.36	694.47	687.72
23.00	722.46	715.70	708.95	702.17	695.35	688.63
24.00	723.13	716.43	709.72	702.97	696.22	689.54
25.00	723.78	717.13	710.48	703.79	697.07	690.43

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}$ mol·mol^{-1}, $u(T)$ = 0.03 K, $u(p)$ = 0.02 MPa, $u(\rho)$ = 0.095 kg·m^{-3}, and the combined expanded uncertainty U_c is $U_c(\rho)$ = 0.2 kg·m^{-3} with a 0.95 level of confidence ($k \approx 2$).

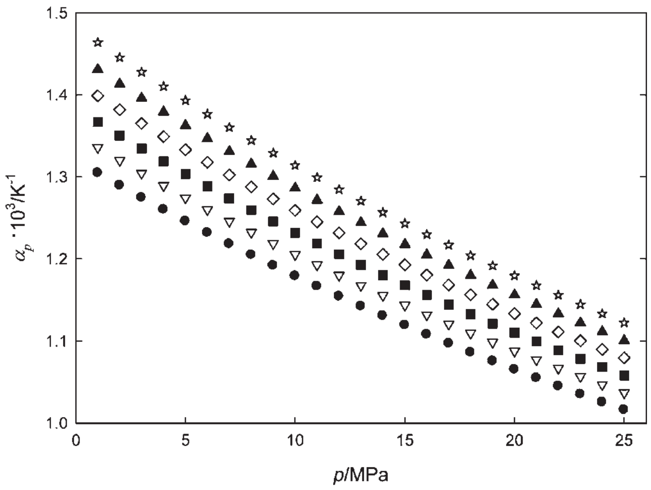

Figure 7. Isobaric thermal expansivity α_p for the hexane (1) + octane (2) system at x_1 = 0.5749: ●, 313.14 K; ▽, 323.06 K; ■, 332.95 K; ◇ 342.93 K; ▲, 352.79 K; ☆, 362.76 K.

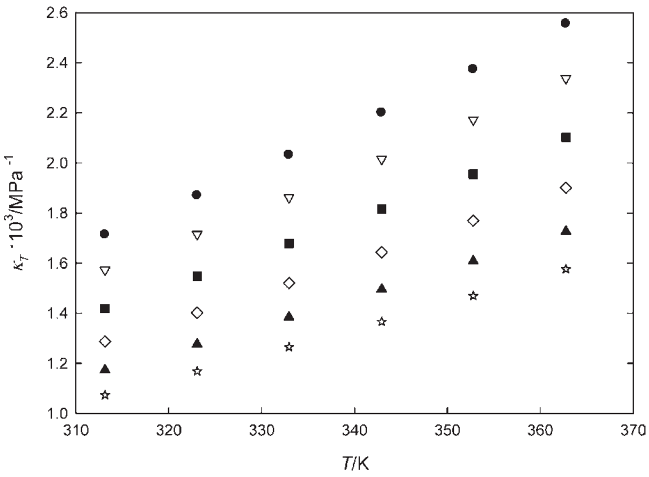

Figure 8. Isothermal compressibility κ_T for the hexane (1) + octane (2) system at x_1 = 0.5749: ●, 1 MPa; ▽, 5 MPa; ■, 10 MPa; ◇, 15 MPa; ▲, 20 MPa; ☆, 25 MPa.

It is a function of the mixture density ρ_M, molecular weight MW, and mole fraction x; subscripts 1 and 2 denote each compound in the binary mixture. The combined uncertainty was estimated to be ± $8.5 \cdot 10^{-5}$ m^3·kmol^{-1}.

Table 9. Experimental Densities for the Binary Mixture Hexane (1) + Decane (2) at $x_1 = 0.4968$[a]

p	$\rho/\mathrm{kg \cdot m^{-3}}$					
MPa	313.21 K	323.14 K	332.58 K	343.08 K	353.01 K	362.94 K
1.00	688.23	679.98	671.98	663.07	654.56	646.01
2.00	689.24	681.03	673.11	664.35	655.89	647.42
3.00	690.26	682.14	674.24	665.55	657.20	648.86
4.00	691.19	683.21	675.37	666.80	658.52	650.21
5.00	692.15	684.24	676.46	667.97	659.83	651.60
6.00	693.12	685.27	677.53	669.14	661.12	652.91
7.00	694.03	686.28	678.61	670.28	662.30	654.20
8.00	694.95	687.29	679.66	671.40	663.52	655.48
9.00	695.84	688.27	680.68	672.48	664.66	656.71
10.00	696.74	689.22	681.70	673.55	665.80	657.94
11.00	697.60	690.14	682.69	674.64	666.94	659.13
12.00	698.47	691.07	683.66	675.64	668.05	660.32
13.00	699.32	691.97	684.64	676.63	669.13	661.45
14.00	700.16	692.85	685.59	677.63	670.21	662.60
15.00	700.95	693.71	686.54	678.63	671.26	663.75
16.00	701.76	694.57	687.44	679.61	672.30	664.81
17.00	702.55	695.40	688.35	680.59	673.30	665.88
18.00	703.34	696.25	689.24	681.52	674.32	666.95
19.00	704.08	697.05	690.12	682.46	675.27	667.98
20.00	704.83	697.87	690.99	683.40	676.25	669.01
21.00	705.58	698.66	691.85	684.32	677.22	670.03
22.00	706.34	699.42	692.69	685.22	678.15	671.04
23.00	707.05	700.17	693.52	686.10	679.08	672.03
24.00	707.76	700.91	694.34	686.98	680.00	673.00
25.00	708.45	701.65	695.13	687.83	680.91	673.96

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}\ \mathrm{mol \cdot mol^{-1}}$, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095\ \mathrm{kg \cdot m^{-3}}$, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2\ \mathrm{kg \cdot m^{-3}}$ with a 0.95 level of confidence ($k \approx 2$).

Table 10. Experimental Densities for the Binary Mixture Hexane (1) + Decane (2) at $x_1 = 0.7524$[a]

p	$\rho/\mathrm{kg \cdot m^{-3}}$					
MPa	313.18 K	323.16 K	333.10 K	343.06 K	352.99 K	362.93 K
1.00	668.32	659.51	650.65	641.66	632.44	623.36
2.00	669.40	660.73	651.99	643.07	633.97	624.97
3.00	670.46	661.92	653.29	644.43	635.47	626.55
4.00	671.50	663.04	654.52	645.80	636.89	628.12
5.00	672.55	664.17	655.72	647.10	638.37	629.63
6.00	673.61	665.29	656.92	648.40	639.77	631.14
7.00	674.58	666.38	658.07	649.65	641.14	632.58
8.00	675.56	667.43	659.21	650.88	642.48	634.03
9.00	676.55	668.50	660.35	652.12	643.77	635.42
10.00	677.50	669.53	661.46	653.31	645.03	636.78
11.00	678.44	670.57	662.52	654.46	646.28	638.11
12.00	679.36	671.56	663.60	655.59	647.51	639.39
13.00	680.27	672.52	664.65	656.72	648.71	640.69
14.00	681.18	673.49	665.67	657.81	649.88	641.96
15.00	682.08	674.44	666.70	658.89	651.03	643.24
16.00	682.96	675.39	667.68	659.96	652.16	644.37
17.00	683.82	676.32	668.66	661.00	653.28	645.56
18.00	684.65	677.22	669.62	662.03	654.35	646.73
19.00	685.47	678.11	670.59	663.03	655.43	647.87
20.00	686.29	678.99	671.52	664.01	656.50	649.00
21.00	687.07	679.85	672.45	664.97	657.54	650.11
22.00	687.87	680.67	673.35	665.93	658.56	651.20
23.00	688.65	681.51	674.23	666.87	659.55	652.27
24.00	689.40	682.33	675.08	667.79	660.56	653.30
25.00	690.14	683.11	675.91	668.69	661.49	654.33

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}\ \mathrm{mol \cdot mol^{-1}}$, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095\ \mathrm{kg \cdot m^{-3}}$, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2\ \mathrm{kg \cdot m^{-3}}$ with a 0.95 level of confidence ($k \approx 2$).

The two binary systems exhibit negative excess molar volumes; near to the equimolar mixture a maximum negative value is shown for each isotherm. As the V^E values have the same behavior for the intermediate temperatures between (313 and 363) K, an example of the temperature and pressure dependence for V^E is plotted in Figure 5 and 6 for each system.

Extrapolated densities at 298.15 K were used to compute the excess molar volumes for both systems with the purpose of knowing the order of magnitude between this work and those reported at equimolar composition by Katzenski and Schneider.[20]

The V^E values[20] and the extrapolated trend for hexane + decane at 20 MPa are within the reported uncertainties. For the hexane + octane system, differences between isobaric trends and data points[20] have differences of about $0.5 \cdot 10^{-3}\ \mathrm{m^3 \cdot kmol^{-1}}$. It could probably be attributed to the purity of chemicals used in the literature[20] because authors do not specify the purity of each chemical clearly.

Derivative properties were calculated using the six-parameter equation and the parameters from Table 12. The isobaric thermal expansivity α_p and isothermal compressibility κ_T are expressed with following expressions:

$$\alpha_p = -\frac{1}{\rho_M}\left(\frac{\partial \rho_M}{\partial T}\right)_p \tag{4}$$

$$\kappa_T = \frac{1}{\rho_M}\left(\frac{\partial \rho_M}{\partial p}\right)_T \tag{5}$$

After solving these derivatives and calculating the numerical value, we proceed to determine their corresponding uncertainties. These were obtained through the law of propagation of errors using the covariance matrix and claimed to be $u(\alpha_p) = 5.6 \cdot 10^{-6}\ \mathrm{K^{-1}}$ and $u(\kappa_T) = 1.0 \cdot 10^{-5}\ \mathrm{MPa^{-1}}$. The isobaric thermal expansivity and isothermal compressibility exhibit the same behavior in both systems. Therefore, an example of each variable is illustrated in Figures 7 and 8 based on the hexane (1) + octane (2) with a fixed composition of $x_1 = 0.5749$. α_p values are plotted against pressure, and κ_T values are plotted in reference to temperature. These properties were found to be proportional to temperature changes at constant pressure; however, these are inverse to pressure changes at isothermal conditions.

Table 11. Experimental Densities for the Binary Mixture Hexane (1) + Decane (2) at $x_1 = 0.8991^a$

p	ρ/kg·m^{-3}					
MPa	313.08 K	322.99 K	332.93 K	342.80 K	352.75 K	362.59 K
1.00	654.30	645.29	636.12	626.74	617.37	607.57
2.00	655.28	646.40	637.35	628.11	618.91	609.29
3.00	656.28	647.52	638.61	629.48	620.43	610.97
4.00	657.30	648.64	639.84	630.85	621.91	612.62
5.00	658.33	649.64	641.09	632.19	623.4	614.24
6.00	659.37	650.89	642.30	633.52	624.85	615.83
7.00	660.42	652.02	643.52	634.85	626.29	617.37
8.00	661.47	653.14	644.74	636.16	627.7	618.92
9.00	662.52	654.27	645.94	637.46	629.09	620.4
10.00	663.56	655.38	647.14	638.73	630.46	621.89
11.00	664.61	656.46	648.32	639.99	631.8	623.32
12.00	665.63	657.57	649.47	641.23	633.12	624.72
13.00	666.66	658.64	650.61	642.43	634.41	626.12
14.00	667.66	659.70	651.73	643.64	635.69	627.49
15.00	668.63	660.74	652.84	644.80	636.93	628.8
16.00	669.61	661.75	653.92	645.95	638.16	630.11
17.00	670.54	662.76	654.97	647.07	639.35	631.37
18.00	671.45	663.71	655.99	648.18	640.52	632.62
19.00	672.34	664.67	657.01	649.24	641.66	633.83
20.00	673.21	665.59	657.98	650.30	642.78	635.04
21.00	674.04	666.49	658.93	651.32	643.87	636.21
22.00	674.91	667.35	659.86	652.31	644.93	637.35
23.00	675.69	668.19	660.76	653.28	645.98	638.45
24.00	676.48	669.02	661.64	654.23	646.99	639.52
25.00	677.31	669.89	662.49	655.16	647.98	640.65

[a] Standard uncertainties are: $u(x_1) = 1 \cdot 10^{-4}$ mol·mol^{-1}, $u(T) = 0.03$ K, $u(p) = 0.02$ MPa, $u(\rho) = 0.095$ kg·m^{-3}, and the combined expanded uncertainty U_c is $U_c(\rho) = 0.2$ kg·m^{-3} with a 0.95 level of confidence ($k \approx 2$).

Table 12. Parameters for the Modified Toscani and Szwarc Equation

	d_1	d_2	d_3	d_4	d_5		AAD
x_1	MPa·m^3·kg^{-1}	m^3·kg^{-1}	MPa	MPa·K^{-1}	MPa·K$^{-1/2}$	d_6	%
			Hexane (1) + Octane (2)				
0.1654	−2.1199	−0.0194	−1750.56	−2.5356	−27.501	−15.506	0.012
0.2199	−2.3097	−0.0217	−1655.44	−3.5323	−57.563	−17.220	0.012
0.5749	−35.610	−0.3644	−26928.29	−52.229	−741.27	−283.94	0.014
0.7995	−36.955	−0.4054	−27213.33	−57.311	−841.22	−310.22	0.015
0.9308	−73.305	−0.8399	−54439.41	−114.49	−1625.13	−637.36	0.016
			Hexane (1) + Decane (2)				
0.0456	−2.2469	−0.0171	−1975.01	−2.3028	−19.602	−14.273	0.005
0.2185	−2.1399	−0.0172	−1875.23	−2.2283	−18.579	−14.171	0.005
0.4968	−2.5470	−0.0238	−2161.39	−2.9828	−29.563	−19.052	0.006
0.7524	−38.0355	−0.4052	−28636.71	−57.0480	−825.164	−314.523	0.007
0.8991	−35.8385	−0.3902	−27170.90	−53.6095	−734.692	−299.37	0.019

■ CONCLUSIONS

Experimental densities are reported for the hexane + octane and hexane + decane systems from (313 to 363) K and up to 25 MPa using a DMA HPM densimeter from Anton Paar based on the static−synthetic method and a data acquisition system. These densities show good agreement against those correlated with the six-parameter equation within the deviation reported for the proposed equations in the studied range. Extrapolated density trends at 0.1 MPa are in agreement with the literature data. The excess molar volumes exhibit maximum negative values at about the intermediate compositions at constant pressure and temperature. Taking into account that the V^E values are quite low and near to zero as the number of carbon atoms for both components are closer, these mixtures are considered to be ideal in particular on the opposite diluted compositions.

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