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Compressed Liquid Densities and Excess Volumes of CO_2 + Decane Mixtures from (313 to 363) K and Pressures up to 25 MPa

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Experimental liquid densities of decane and of CO_2 (1) + decane (2) binary mixtures (at five different compositions, $x_1 = 0.0551$, 0.2369, 0.4536, 0.8114, and 0.9663) were measured from (313 to 363) K and at pressures up to 25 MPa. The densities of decane were fitted to the Benedict−Webb−Rubin−Starling equation of state (BWRS EoS). Excess molar volumes are calculated by using decane densities calculated from the BWRS EoS and CO_2 densities calculated from the Span−Wagner EoS.

Introduction

Sulfur content lower limits in fuels have become a source of new investigations all around the world. At present, a hydrotreating process is used to obtain low sulfur content fuels; however, energy and hydrogen consumption will make this process undesirable. Alternative processes, such as extraction using supercritical fluids and ionic liquids, are needed. An attempt to develop a new sulfur extraction process was recently made by Huang et al.[1] They used dodecane and thiophene as a model diesel to perform sulfur extraction using ionic liquids. This work is part of a project focused on sulfur compound extraction from commercial fuels using supercritical carbon dioxide[2,3] to fulfill sulfur content regulations.[1] Because decane is a component present in fuels, it can be used as a model fuel as Huang et al.[1] did with dodecane.

The development of supercritical fluid extraction processes is strongly dependent on accurate thermodynamic data as *PVT* properties and phase equilibria of pure compounds and mixtures. In this work, the volumetric behavior of CO_2 + decane were determined as basic information for process development and as part of a systematic study.[2,3] This system has been previously reported in the literature. Cullick and Mathis[4] measured the density of CO_2 (1) + decane (2) from (310 to 403) K and (7 to 30) MPa and at $x_1 = 0.15$, 0.301, 0.505, 0.649, and 0.85. Bessiéres et al.[5] measured the density of this system from (308.15 to 368.15 K) and (20 to 40) MPa and at $x_1 = 0.16$, 0.22, 0.34, 0.49, 0.70, and 0.85. In this work, new experimental densities for decane and for CO_2 (1) + decane (2) mixtures from (313 to 363) K and up to 25 MPa at $x_1 = 0.0551$, 0.2369, 0.4536, 0.8114, and 0.9663 are reported.

Experimental Section

Materials. The sources and purities of the various compounds are given in Table 1. These materials were used without any further purification, except for careful degassing of water and decane.

Table 1. Purity and Origin of Pure Compounds

compound	certified purity	supplier
decane	99 + mole % anhydrous	Aldrich
CO_2	99.995 mole %	Air Products-Infra
water	99.95 mole % (HPLC)	Aldrich
nitrogen	99.998 mole %	Air Products-Infra

Apparatus and Procedure. The apparatus and experimental procedure used in this work have been described previously.[6−9] The measuring cell consists of a vibrating tube (Hastelloy C-276 U-tube) containing a sample of approximately 1 cm^3. The pressure measurements are made directly in the equilibrium cell (Figure 1) by means of a 25 MPa Sedeme pressure transducer. The pressure transducer is thermoregulated at a specific value and calibrated periodically. The temperature was measured by two platinum probes located at the top of the sapphire cell and in the vibrating tube densimeter (VTD). The calibration of the vibrating tube was performed using water and nitrogen as the reference compounds. Density values for

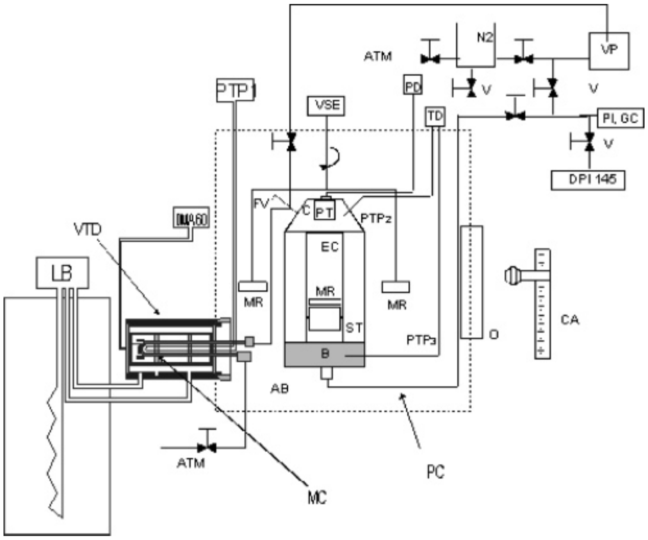

Figure 1. Flow diagram of the apparatus: AB air bath, CA cathetometer, DMA 60 period meter, DPI 145 digital indicator of pressure, EC equilibrium cell, GC gas compressor, LB liquid bath, MC measurement cell, MR magnetic rod, PI Isco pump, PT pressure transducer, PTP*i* platinum probe *i*, TD digital indicator of temperature F250, V*i* shut-off valve *i*, VSE variable-speed engine, VP vacuum pump, VTD vibrating tube densimeter, O window.

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Table 2. BWRS EOS Adjusted Parameters for Decane

parameter	decane
B_0/cm^3·mol^{-1}	653.40
A_0/bar·cm^6·mol^{-2}	4.9923×10^7
C_0/bar·K^2·cm^6·mol^{-2}	2.82531×10^{12}
D_0/bar·K^3·cm^6·mol^{-2}	-5.470013×10^{14}
E_0/bar·K^4·cm^6·mol^{-2}	-1.954206×10^{17}
b/cm^6·mol^{-2}	129 382.289
a/bar·cm^9·mol^{-3}	2.77188×10^9
d/bar·K·cm^9·mol^{-3}	4.89128×10^{11}
c/bar·K^2·cm^9·mol^{-3}	-7.00804×10^{14}
α/cm^9·mol^{-3}	3.39814×10^7
u/cm^6·mol^{-2}	10 090.4141

Table 3. Coefficients for the Lemmon−Span EoS[14] for Decane

coefficient	decane
n_1	1.0461
n_2	−2.4807
n_3	0.74372
n_4	−0.52579
n_5	0.15315
n_6	0.00032865
n_7	0.84178
n_8	0.055424
n_9	−0.73555
n_{10}	−0.18507
n_{11}	−0.020775
n_{12}	0.012335

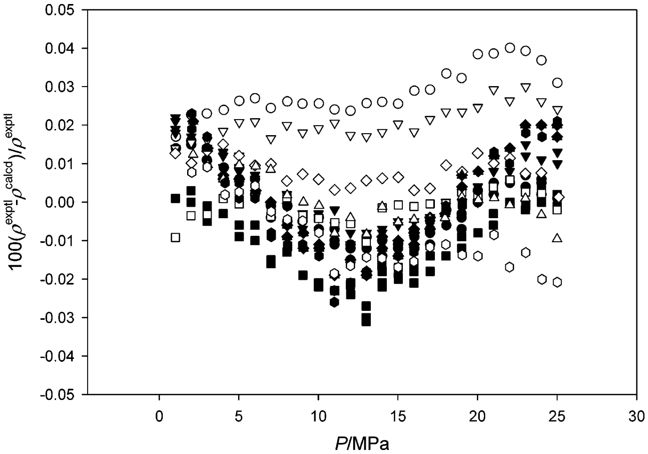

Figure 2. Relative deviations between experimental densities of decane and those calculated with the BWRS EoS and the Lemmon−Span EoS at the following temperatures: ●, 313.09 K; ▼, 323.03 K; ■, 332.95 K; ◆, 342.80; ▲, 352.71 K; ●, 362.63 K. Closed and open symbols are for deviations using the BWRS EoS and the Lemmon−Span EoS, respectively.

water and nitrogen were obtained from the equations proposed by Wagner and Pruβ[10] and Span et al.,[11] respectively. Details about the calibrating procedures of the platinum temperature probes and the pressure transducer were given in a previous article.[12] The estimated uncertainties of the experimental quantities presented in this work are T/K = ±0.03, P/MPa = ±0.008, and ρ/kg·m^{-3} = ±0.2 for liquid density in the range of the reported data, in a similar fashion as previously reported data.[7−9]

Loading of the Measurement Cell. A detailed procedure of the loading of the measurement cell is presented in preceding papers.[6,9] The samples with the desired compositions are prepared by successive loadings[6] of the pure compounds in a sapphire feeding cell with a maximum volume of 12 cm^3. The amounts of the compounds are determined by weighing carried out with an uncertainty of ±10^{-7} kg with a Sartorius comparator balance (MCA1200), which was periodically calibrated with a standard mass of 1 kg class E1. The resulting uncertainty for the mole fraction composition of the mixtures is lower than ±10^{-4}.

Theory. The BWRS EoS[13] was used to correlate the densities of decane. The following expression was used:

$$P = \frac{RT}{V} + \frac{(B_0RT - A_0 - C_0/T^2 + D_0/T^3 - E_0/T^4)}{V^2} + \frac{(bRT - a - d/T)}{V^3} + \frac{\alpha(a + d/T)}{V^6} + \frac{c(1 + u/V^2)\exp(-u/V^2)}{V^3T^2} \tag{1}$$

where V is the molar volume and the units for the corresponding constants are shown in Table 2.

Table 4. Experimental Densities of Decane

P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}
T/K = 313.09		T/K = 323.03		T/K = 332.95		T/K = 342.80		T/K = 352.71		T/K = 362.63	
1.048	715.63	1.025	707.94	1.022	700.40	1.014	692.56				
2.010	716.43	2.017	708.85	2.005	701.33	2.027	693.64	2.132	686.04	2.054	678.23
2.997	717.28	3.015	709.76	3.025	702.32	3.016	694.64	3.053	687.07	3.010	679.34
4.060	718.18	4.018	710.65	4.025	703.25	4.020	695.65	4.028	688.15	4.132	680.68
5.029	718.98	5.022	711.53	5.018	704.20	5.016	696.67	5.028	689.19	5.020	681.68
6.019	719.80	6.021	712.41	6.018	705.12	6.019	697.68	6.065	690.28	6.026	682.79
7.016	720.64	7.018	713.31	7.019	706.08	7.026	698.66	7.007	691.26	7.042	683.95
8.050	721.47	8.022	714.15	8.023	706.96	8.022	699.65	8.041	692.36	8.057	685.06
9.000	722.24	9.016	715.01	9.021	707.89	9.014	700.58	9.064	693.40	9.014	686.08
10.029	723.06	10.012	715.84	10.017	708.78	10.017	701.53	10.047	694.38	10.034	687.17
11.016	723.85	11.022	716.67	11.033	709.68	11.022	702.48	11.019	695.38	10.999	688.24
12.012	724.63	12.015	717.51	12.023	710.54	12.021	703.39	12.012	696.31	12.014	689.26
13.027	725.40	13.020	718.33	13.009	711.42	13.011	704.27	13.031	697.31	13.025	690.26
14.011	726.15	14.011	719.12	14.016	712.21	14.013	705.16	14.010	698.18	13.992	691.22
15.010	726.91	15.010	719.90	15.025	713.05	15.025	706.05	15.014	699.14	15.019	692.24
16.030	727.65	16.019	720.71	16.011	713.87	16.019	706.94	16.012	700.05	16.004	693.18
17.016	728.38	17.010	721.46	17.017	714.69	17.010	707.79	17.008	700.95	17.008	694.11
18.037	729.10	18.013	722.22	18.016	715.50	18.023	708.61	17.959	701.80	18.002	695.04
19.000	729.81	19.033	723.00	19.015	716.28	19.030	709.47	19.020	702.70	19.037	696.02
20.019	730.50	20.022	723.74	20.029	717.09	20.008	710.25	20.044	703.60	20.027	696.93
21.014	731.21	21.014	724.45	21.001	717.84	21.017	711.10	21.044	704.46	21.030	697.80
22.032	731.92	22.023	725.22	22.034	718.63	22.035	711.92	22.024	705.31	22.003	698.73
23.021	732.62	23.025	725.93	23.017	719.41	23.004	712.73	23.009	706.13	23.027	699.61
24.016	733.33	24.016	726.68	24.023	720.18	24.008	713.53	24.014	707.00	24.046	700.55
25.012	734.06	25.021	727.42	25.002	720.95	25.103	714.44	25.000	707.86	25.011	701.39

Table 5. Comparison of Densities between Literature Data and Calculated Values by the BWRS EoS

T/K	P/MPa	ρ/kg·m^{-3} (ref 5)	$100(\rho^{\text{ref 5}} - \rho^{\text{BWRS}})/\rho^{\text{ref 5}}$
308.15	20	734.79	0.127
318.15	20	727.82	0.104
328.15	20	720.92	0.090
338.15	20	714.02	0.076
348.15	20	707.19	0.069
358.15	20	700.30	0.050
368.15	20	693.35	0.020
308.15	30	741.46	0.105
318.15	30	734.79	0.075
328.15	30	728.22	0.055
338.15	30	721.72	0.040
348.15	30	715.26	0.027
358.15	30	708.80	0.008
368.15	30	702.31	−0.020
308.15	40	747.57	0.064
318.15	40	741.14	0.024
328.15	40	734.84	−0.004
338.15	40	728.65	−0.022
348.15	40	722.52	−0.039
358.15	40	716.42	−0.059
368.15	40	710.33	−0.083

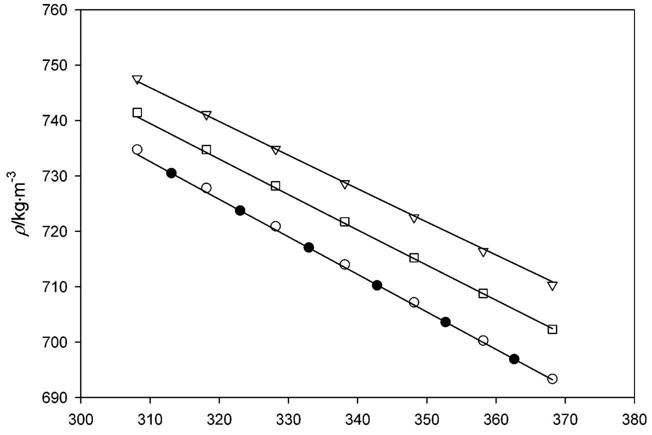

Figure 3. Experimental and calculated densities of decane: ●, this work at 20 MPa; ○, Bessières et al.[5] at 20 MPa; □, Bessières et al.[5] at 30 MPa; ▽, Bessières et al.[5] at 40 MPa;−, BWRS EoS.

The equation of state proposed by Lemmon and Span[14] was used to calculate the densities reported here. Density was calculated from the expression

$$P = \rho RT\left[1 + \delta\left(\frac{\partial \alpha^{r}}{\partial \delta}\right)_{\tau}\right] \qquad (2)$$

Table 6. Experimental Densities and Excess Molar Volumes of the CO$_2$ (1) + Decane (2) Mixture

P/MPa	ρ/kg·m^{-3}	V^{E}/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^{E}/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^{E}/cm^3·mol^{-1}
				x_1 = 0.0551				
	T/K = 313.10			T/K = 323.05			T/K = 332.94	
2.005	717.94	−62.13	1.989	710.33	−65.47	1.997	702.61	−67.83
3.035	718.98	−37.65	3.015	711.28	−39.99	3.024	703.63	−41.78
4.061	719.88	−25.45	3.984	712.18	−27.88	4.011	704.59	−29.24
5.063	720.72	−18.13	5.002	713.14	−20.12	5.040	705.62	−21.35
6.029	721.55	−13.20	6.010	714.04	−14.91	6.062	706.62	−16.09
7.028	722.42	−9.24	7.043	714.97	−10.98	7.009	707.53	−12.53
7.998	723.25	−5.84	8.018	715.86	−8.06	7.978	708.43	−9.69
9.019	724.09	−2.05	9.009	716.73	−5.55	9.037	709.44	−7.22
10.010	724.92	−1.00	10.008	717.66	−3.38	9.992	710.31	−5.38
11.032	725.72	−0.69	11.036	718.47	−1.88	11.032	711.27	−3.75
12.046	726.55	−0.54	11.995	719.35	−1.27	12.013	712.13	−2.60
13.029	727.32	−0.43	13.035	720.16	−0.92	13.027	713.03	−1.83
14.011	728.10	−0.36	14.026	721.01	−0.74	14.018	713.89	−1.38
15.013	728.84	−0.29	15.008	721.76	−0.60	15.021	714.75	−1.09
15.992	729.58	−0.24	16.035	722.62	−0.50	15.997	715.59	−0.89
16.999	730.32	−0.19	17.008	723.40	−0.43	16.998	716.44	−0.75
18.044	731.13	−0.16	18.019	724.22	−0.37	18.031	717.29	−0.63
19.030	731.85	−0.12	18.994	724.89	−0.29	19.004	718.07	−0.53
19.999	732.57	−0.10	20.009	725.73	−0.26	20.002	718.88	−0.46
21.031	733.30	−0.06	21.010	726.47	−0.21	21.014	719.68	−0.39
22.015	734.00	−0.04	21.987	727.22	−0.18	22.027	720.50	−0.34
23.023	734.74	−0.02	23.060	728.04	−0.15	23.014	721.30	−0.29
24.060	735.50	0.00	23.980	728.74	−0.12	24.057	722.11	−0.25
25.026	736.20	0.01	25.055	729.61	−0.11	25.048	722.92	−0.22
	T/K = 342.86			T/K = 352.78			T/K = 362.66	
2.043	694.82	−68.64	2.008	686.89	−72.53	2.031	678.97	−74.09
3.006	695.92	−43.98	3.010	688.04	−45.70	3.029	680.17	−47.11
4.043	696.93	−30.47	4.018	689.18	−32.19	4.134	681.50	−32.42
5.044	697.98	−22.68	5.014	690.28	−24.15	5.034	682.58	−25.22
6.046	699.02	−17.42	6.015	691.42	−18.74	6.050	683.77	−19.65
6.984	699.98	−13.84	7.011	692.46	−14.86	7.045	684.91	−15.75
8.003	701.00	−10.86	8.024	693.62	−11.92	8.030	686.02	−12.83
8.999	702.09	−8.61	8.988	694.56	−9.68	9.020	687.12	−10.54
10.007	702.98	−6.71	10.035	695.65	−7.75	10.044	688.25	−8.64
11.044	703.97	−5.15	11.021	696.68	−6.29	11.025	689.34	−7.18
11.996	704.89	−3.98	12.025	697.67	−5.05	11.987	690.35	−5.98
13.021	705.84	−3.00	13.009	698.59	−4.04	13.025	691.46	−4.91
13.997	706.74	−2.30	14.003	699.60	−3.24	14.075	692.50	−4.01
15.043	707.69	−1.78	15.017	700.50	−2.58	15.026	693.52	−3.37
16.022	708.54	−1.43	16.009	701.58	−2.14	16.020	694.47	−2.79
17.001	709.54	−1.22	17.043	702.49	−1.74	17.003	695.45	−2.34
17.984	710.28	−0.99	18.011	703.38	−1.46	18.032	696.46	−1.97
19.042	711.19	−0.84	18.999	704.26	−1.24	19.030	697.38	−1.67
20.017	712.03	−0.72	19.980	705.14	−1.06	19.998	698.32	−1.44
21.054	713.10	−0.67	21.012	706.06	−0.91	21.052	699.32	−1.24
22.022	713.72	−0.54	22.017	706.96	−0.80	22.028	700.22	−1.08
23.029	714.55	−0.47	23.034	707.84	−0.69	22.996	701.10	−0.95
24.018	715.37	−0.41	24.044	708.75	−0.61	24.036	702.10	−0.84
25.025	716.21	−0.36	24.991	709.57	−0.55	25.008	702.93	−0.73

Table 7. Experimental Densities and Excess Molar Volumes of the CO_2 (1) + Decane (2) Mixture

P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
				$x_1 = 0.2369$				
	T/K = 313.10			T/K = 323.06			T/K = 332.94	
5.020	728.09	−79.24	5.014	719.60	−86.24	5.026	711.09	−92.08
6.029	729.09	−56.88	6.022	720.66	−63.92	6.015	712.23	−69.98
7.015	730.07	−40.04	7.021	721.73	−47.59	7.019	713.38	−53.62
8.019	731.05	−24.88	8.020	722.80	−34.66	8.020	714.47	−41.11
9.012	732.01	−9.00	9.010	723.79	−23.85	9.017	715.56	−31.11
10.012	732.96	−4.35	10.030	724.84	−14.29	10.015	716.65	−22.87
11.018	733.88	−3.08	11.018	725.81	−8.15	11.009	717.69	−16.15
12.009	734.80	−2.41	12.021	726.78	−5.35	12.015	718.74	−11.07
13.016	735.72	−1.96	13.001	727.75	−4.01	13.015	719.76	−7.81
14.019	736.60	−1.63	14.021	728.70	−3.17	14.011	720.77	−5.85
15.006	737.46	−1.38	15.014	729.63	−2.61	15.003	721.75	−4.62
16.017	738.34	−1.16	16.010	730.54	−2.19	16.019	722.73	−3.76
17.006	739.17	−0.99	17.006	731.46	−1.87	17.015	723.70	−3.15
18.008	740.01	−0.84	18.028	732.36	−1.60	18.026	724.66	−2.68
19.016	740.85	−0.70	19.016	733.24	−1.39	19.022	725.60	−2.31
20.000	741.67	−0.59	20.015	734.11	−1.20	20.012	726.51	−2.00
21.019	742.51	−0.49	21.027	735.00	−1.04	21.024	727.44	−1.75
22.002	743.29	−0.40	22.023	735.85	−0.90	22.021	728.35	−1.54
23.007	744.12	−0.32	23.022	736.71	−0.78	23.010	729.26	−1.35
24.008	744.96	−0.26	24.006	737.58	−0.68	24.025	730.17	−1.19
25.013	745.78	−0.20	25.004	738.42	−0.59	25.028	731.08	−1.05
	T/K = 342.87			T/K = 352.79			T/K = 362.65	
5.031	702.48	−97.71						
6.026	703.70	−75.13	6.023	695.17	−80.15	5.978	686.43	−85.64
7.029	704.93	−58.70	7.016	696.39	−63.56	7.016	687.86	−67.84
8.006	706.09	−46.52	8.017	697.70	−50.96	8.020	689.21	−54.99
9.030	707.28	−36.45	9.014	698.95	−41.14	9.035	690.58	−44.90
10.017	708.40	−28.62	10.006	700.10	−33.26	10.044	691.88	−36.89
11.019	709.54	−22.10	11.019	701.32	−26.73	11.011	693.13	−30.64
12.003	710.62	−16.91	12.015	702.48	−21.46	12.005	694.38	−25.32
13.017	711.73	−12.74	13.014	703.71	−17.16	13.039	695.64	−20.75
14.013	712.79	−9.72	14.010	704.77	−13.70	14.013	696.82	−17.22
15.021	713.84	−7.56	15.002	705.93	−11.02	15.072	698.07	−14.07
16.004	714.86	−6.09	16.000	707.03	−8.95	16.012	699.18	−11.82
17.018	715.90	−4.99	17.020	708.08	−7.33	17.009	700.33	−9.89
18.016	716.89	−4.19	18.006	709.15	−6.15	18.008	701.44	−8.34
19.005	717.86	−3.58	19.014	710.21	−5.22	19.020	702.57	−7.10
20.000	718.83	−3.09	19.955	711.22	−4.53	20.006	703.64	−6.12
21.023	719.83	−2.69	21.069	712.30	−3.86	21.068	704.82	−5.27
22.008	720.78	−2.36	22.042	713.30	−3.39	22.007	705.81	−4.65
23.029	721.76	−2.08	23.032	714.28	−2.99	23.055	706.93	−4.08
23.992	722.74	−1.87	24.057	715.33	−2.65	24.030	707.95	−3.63
25.008	723.65	−1.65	24.999	716.29	−2.39	25.056	709.02	−3.23

where $\alpha^r(\delta, \tau)$ is given by[14]

$$\alpha^r(\delta, \tau) = n_1\delta\tau^{0.25} + n_2\delta\tau^{1.125} + n_3\delta\tau^{1.5} + n_4\delta^2\tau^{1.375} + n_5\delta^3\tau^{0.25} + n_6\delta^7\tau^{0.875} + n_7\delta^2\tau^{0.625}\exp^{-\delta} + n_8\delta^5\tau^{1.75}\exp^{-\delta} + n_9\delta\tau^{3.625}\exp^{-\delta^2} + n_{10}\delta^4\tau^{3.625}\exp^{-\delta^2} + n_{11}\delta^3\tau^{14.5}\exp^{-\delta^3} + n_{12}\delta^4\tau^{12.0}\exp^{-\delta^3} \quad (3)$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$. Constants n_1 to n_{12} are listed in Table 3.

To make comparisons with reported literature data,[4,5] we propose a five-parameter empirical equation to correlate the densities of decane and those of the CO_2 + decane mixtures.

$$\nu = \frac{c_1 + c_2P}{c_3 - (c_4/T + c_5/T^{1/3}) + P} \quad (4)$$

where different sets of c_1, c_2, c_3, c_4, and c_5 were obtained by fitting experimental data for the different compositions of the mixtures and for decane reported in this work.

Results and Discussion

Densities of decane are reported in Table 4. The parameters of the BWRS EoS[13] were fitted to the experimental densities of decane reported in this work. The Marquardt−Levenberg least-squares optimization was used with the following objective function, S:

$$S = \sum_i \left[\frac{\rho_i^{\text{exptl}} - \rho_i^{\text{calcd}}}{\rho_i^{\text{exptl}}}\right]^2 \quad (5)$$

The BWRS EoS[13] adjusted parameters for decane are reported in Table 2. Densities of decane from the BWRS EoS were calculated with a standard deviation of 0.0242%. Relative deviations using eqs 1 and 2 are plotted in Figure 2. The average absolute deviation in density using the Lemmon−Span EoS[14] was about 0.01%.

Data for decane from this work and from Bessiéres et al.[5] at 20 MPa are plotted in Figure 3; good agreement between both sets of data is observed. The adjusted parameters for the BWRS EoS[13] were tested by predicting the densities of decane reported by Bessiéres et al.[5] at (30 and 40) MPa. These results are plotted in Figure 3, and the corresponding deviations are reported in Table 5. The predicted values are in good agreement with experimental data.

In Tables 6 to 10, compressed liquid densities and excess molar volumes for the CO_2 + decane mixtures at temperatures from (313 to 363) K and pressures up to 25 MPa at five different compositions are presented.

Table 8. Experimental Densities and Excess Molar Volumes of the CO_2 (1) + Decane (2) Mixture

P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
				$x_1 = 0.4536$				
	T/K = 313.11			T/K = 323.06			T/K = 332.94	
7.015	742.30	−76.55	7.029	732.05	−90.66	7.015	721.74	−102.46
8.024	743.57	−47.38	8.017	733.42	−66.22	8.025	723.26	−78.30
9.021	744.82	−16.96	9.018	734.79	−45.30	9.016	724.72	−59.30
10.024	746.02	−8.18	10.024	736.13	−27.24	10.023	726.15	−43.39
11.020	747.22	−5.80	11.019	737.41	−15.40	11.014	727.55	−30.62
12.022	748.39	−4.52	12.025	738.69	−10.06	12.001	728.90	−21.08
13.012	749.55	−3.68	13.003	739.89	−7.51	13.045	730.28	−14.59
14.017	750.69	−3.05	14.027	741.16	−5.91	13.998	731.55	−11.04
15.020	751.81	−2.57	15.001	742.33	−4.88	15.000	732.81	−8.65
16.020	752.93	−2.18	16.024	743.53	−4.07	16.032	734.14	−7.01
17.013	753.99	−1.86	17.010	744.68	−3.47	17.018	735.36	−5.87
18.019	755.06	−1.58	18.030	745.84	−2.97	18.021	736.57	−4.99
19.014	756.08	−1.34	19.000	746.93	−2.58	19.012	737.79	−4.30
20.018	757.13	−1.14	20.028	748.09	−2.24	20.002	738.93	−3.73
21.018	758.18	−0.96	21.001	749.17	−1.95	21.028	740.14	−3.25
22.006	759.18	−0.80	22.020	750.24	−1.69	22.021	741.29	−2.86
23.003	760.18	−0.65	23.012	751.33	−1.47	23.009	742.44	−2.53
24.023	761.23	−0.53	24.021	752.42	−1.28	24.026	743.58	−2.23
25.010	762.23	−0.42	25.029	753.51	−1.11	25.022	744.71	−1.97
	T/K = 342.87			T/K = 352.80			T/K = 362.66	
7.027	711.28	−112.01						
8.024	712.92	−88.29	8.029	702.49	−96.80			
9.027	714.50	−69.46	9.011	704.17	−78.32	9.024	693.68	−85.54
10.014	716.02	−54.46	10.022	705.86	−63.05	10.012	695.47	−70.49
11.025	717.56	−41.91	11.012	707.47	−50.85	11.031	697.25	−57.88
12.015	719.02	−31.95	12.018	709.07	−40.69	12.002	698.93	−47.99
13.006	720.46	−24.16	13.013	710.62	−32.49	13.028	700.66	−39.35
14.013	721.87	−18.33	14.019	712.14	−25.85	14.008	702.25	−32.54
15.001	723.23	−14.29	15.017	713.63	−20.71	15.024	703.87	−26.77
16.029	724.63	−11.36	16.008	715.06	−16.80	16.000	705.42	−22.29
17.019	725.94	−9.34	17.028	716.51	−13.76	17.017	706.96	−18.55
18.026	727.26	−7.83	18.018	717.90	−11.51	18.002	708.44	−15.66
19.018	728.54	−6.68	19.024	719.28	−9.75	19.030	709.94	−13.26
20.000	729.75	−5.77	20.015	720.60	−8.38	20.001	711.37	−11.45
21.007	731.02	−5.03	21.003	721.91	−7.28	21.029	712.80	−9.89
22.021	732.28	−4.41	22.029	723.29	−6.36	22.014	714.18	−8.67
23.032	733.50	−3.88	23.006	724.51	−5.62	23.024	715.57	−7.63
24.017	734.70	−3.45	24.025	725.86	−4.98	24.006	716.91	−6.79
25.029	735.91	−3.07	25.013	727.09	−4.45	25.025	718.29	−6.04

The excess volumes were calculated over the complete temperature and pressure intervals according to the relation

$$V^E = \frac{x_1W_1 + x_2W_2}{\rho^{\text{mix}}} - (x_1V_1 + x_2V_2) \qquad (6)$$

where V^E is the molar excess volume, ρ^{mix} is the density of the mixture, V_1 and V_2 are the pure component molar volumes at the measured temperature and pressure of the mixture, W_1 and W_2 are the molecular weights of CO_2 and decane, respectively, and x_1 and x_2 are the mole fractions of CO_2 and decane, respectively. Densities of decane were calculated in the reported range of pressure and temperature by using the BWRS EoS with the parameters reported in Table 2. The equation of state proposed by Span and Wagner[15] was used to calculate the molar volumes of CO_2. The uncertainty in the excess molar volumes is estimated to be ±0.15%. A typical behavior of the excess molar volume for this type of mixture is shown in Figure 4, where the excess molar volumes is plotted as a function of x_1 at 362.65 K at different pressures. The excess molar volume becomes less negative with increasing pressure, as previously reported.[5]

The reliability of the measurements has been checked by comparing the data calculated through the proposed empirical equation of state fitted to data reported in this work and data from other authors.[4] To compare our experimental data with those reported in the literature, densities for the mixtures reported here and those reported by Cullick and Mathis[4] were correlated at constant composition using eq 4. The obtained parameters, temperature and pressure intervals, data points used for the correlation, and the different statistical values used to evaluate the correlations are reported in Tables 11 and 12. Densities reported by Bessiéres et al.[5] at 20 MPa were taken as a

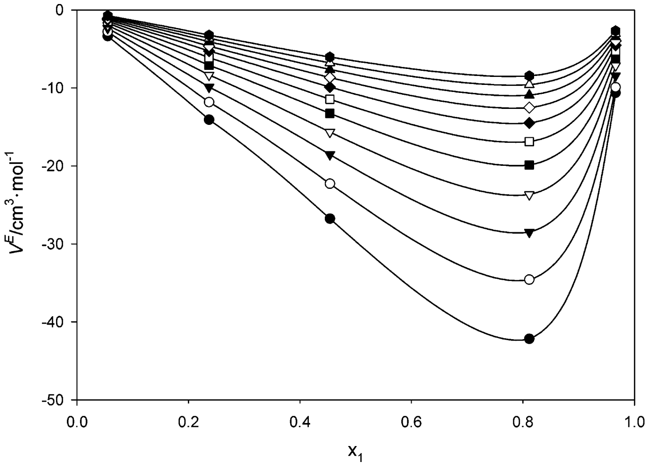

Figure 4. Excess molar volumes of the carbon dioxide (1) + decane (2) binary mixtures at 362.65 K reported in this work: ●, 15 MPa; ○, 16 MPa; ▼, 17 MPa; ▽, 18 MPa; ■, 19 MPa; □, 20 MPa; ◆, 21 MPa; ◇, 22 MPa; ▲, 23 MPa; △, 24 MPa; ●, 25 Mpa;−, trend.

Table 9. Experimental Densities and Excess Molar Volumes of the CO_2 (1) + Decane (2) Mixture

P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
				$x_1 = 0.8114$				
	T/K = 313.12			T/K = 323.04			T/K = 332.91	
12.053	782.82	−6.76	12.005	762.12	−16.20	12.008	740.55	−34.85
13.017	785.68	−5.41	13.009	765.56	−11.65	13.051	744.82	−23.56
14.021	788.54	−4.39	14.026	769.00	−8.97	14.018	748.57	−17.34
15.103	791.51	−3.56	15.008	772.02	−7.21	15.048	752.37	−13.21
15.990	793.84	−3.02	16.046	775.13	−5.88	15.985	755.64	−10.70
16.981	796.39	−2.52	17.018	777.99	−4.93	17.015	759.04	−8.70
17.993	798.92	−2.09	18.002	780.75	−4.17	18.008	762.27	−7.28
19.038	801.45	−1.72	19.025	783.58	−3.53	19.002	765.33	−6.16
20.009	803.73	−1.43	20.031	786.22	−3.00	20.017	768.38	−5.25
21.018	806.06	−1.16	21.047	788.86	−2.56	21.018	771.25	−4.51
22.020	808.29	−0.93	21.988	791.16	−2.19	22.044	774.13	−3.89
22.999	810.42	−0.73	22.999	793.66	−1.87	23.040	776.83	−3.38
24.019	812.60	−0.54	24.016	796.11	−1.58	24.008	779.40	−2.95
25.017	814.70	−0.38	25.054	798.55	−1.32	25.047	782.09	−2.55
	T/K = 342.84			T/K = 352.76			T/K = 362.63	
13.020	721.51	−39.52						
14.001	726.31	−29.67	14.034	701.72	−41.53			
15.022	730.92	−22.50	15.050	707.51	−32.67	15.022	681.16	−42.19
16.041	735.26	−17.59	15.994	712.45	−26.38	16.023	688.18	−34.60
17.013	739.14	−14.27	17.009	717.35	−21.26	17.027	694.15	−28.49
18.018	742.96	−11.75	18.024	722.02	−17.43	18.027	699.67	−23.69
19.020	746.57	−9.85	19.033	726.33	−14.54	19.028	704.83	−19.89
20.008	749.98	−8.39	20.039	730.42	−12.29	20.026	709.67	−16.89
21.023	753.35	−7.19	21.009	734.16	−10.58	21.017	714.17	−14.50
22.003	756.46	−6.25	22.013	737.84	−9.14	22.023	718.48	−12.53
23.041	759.67	−5.42	23.004	741.32	−7.97	23.019	722.51	−10.92
24.026	762.58	−4.76	24.035	744.84	−6.97	24.030	726.42	−9.58
25.034	765.48	−4.18	25.042	748.08	−6.14	25.024	730.11	−8.46

Table 10. Experimental Densities and Excess Molar Volumes of the CO_2 (1) + Decane (2) Mixture

P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
				$x_1 = 0.9663$				
	T/K = 313.11			T/K = 323.04			T/K = 332.94	
11.029	714.21	−2.43	11.016	580.54	−9.15	12.005	511.90	−11.54
12.037	738.68	−1.68	12.030	636.15	−4.59	12.511	544.43	−9.37
13.049	758.54	−1.35	13.015	672.02	−2.91	13.003	571.24	−7.59
14.020	774.43	−1.17	14.007	698.83	−2.10	14.015	614.37	−5.05
15.013	788.48	−1.05	15.021	721.04	−1.68	15.026	648.23	−3.77
16.007	800.98	−0.99	16.018	739.12	−1.42	16.035	674.85	−3.00
17.027	812.43	−0.94	17.026	754.76	−1.25	17.018	695.62	−2.47
17.984	822.21	−0.91	18.010	768.22	−1.14	18.016	713.48	−2.09
19.037	832.11	−0.90	19.001	780.23	−1.06	19.002	728.62	−1.80
20.002	840.48	−0.89	20.025	791.43	−0.99	20.033	742.59	−1.58
21.015	848.66	−0.88	21.021	801.33	−0.94	21.022	754.63	−1.42
22.023	856.28	−0.88	22.023	810.55	−0.90	22.029	765.58	−1.27
23.021	863.40	−0.88	23.026	819.05	−0.86	23.010	775.39	−1.16
24.063	870.36	−0.88	24.036	827.07	−0.84	24.016	784.64	−1.06
24.976	876.18	−0.88	25.030	834.47	−0.82	25.006	793.10	−0.98
	T/K = 342.79			T/K = 352.75			T/K = 362.65	
13.528	503.61	−10.75						
14.029	528.33	−9.40	14.010	449.95	−11.82			
15.026	569.49	−7.02	15.010	494.40	−9.99	15.510	452.61	−10.63
16.019	603.24	−5.43	16.020	532.74	−8.11	16.012	471.04	−9.92
17.025	631.60	−4.36	17.024	566.61	−6.78	17.007	504.42	−8.45
18.035	657.54	−3.84	18.026	594.54	−5.61	18.010	534.34	−7.14
19.000	674.01	−3.01	19.015	618.22	−4.71	19.013	561.23	−6.11
20.022	691.29	−2.55	20.016	638.64	−3.97	20.015	585.01	−5.26
21.024	706.16	−2.20	21.018	656.61	−3.40	21.029	606.13	−4.54
22.022	719.34	−1.91	22.006	672.26	−2.94	22.007	624.31	−3.97
23.022	731.24	−1.68	23.021	686.58	−2.55	23.022	641.03	−3.46
24.017	741.98	−1.49	24.018	699.34	−2.24	24.015	655.59	−3.03
25.006	751.96	−1.34	25.017	710.94	−1.98	25.028	669.28	−2.68

reference, and then the densities at the same temperature and pressure were calculated for the different compositions reported here and in ref 4 with the parameters reported in Tables 11 and 12 for eq 4. Good agreement exists among the three sets of data, as shown in Figure 5.

Conclusions

In this work, we reported new compressed liquid densities of decane and CO_2 + decane mixtures covering the whole interval of composition at temperatures from (313

Table 11. Parameters for Equation 4 for Data Reported in This Work[a]

	$x_1 = 0$	$x_1 = 0.0551$	$x_1 = 0.2369$	$x_1 = 0.4536$	$x_1 = 0.8114$	$x_1 = 0.9663$
$T_{\min}$/K	313.09	313.10	313.10	313.11	313.12	313.11
$T_{\max}$/K	352.62	362.66	362.65	362.66	362.63	362.65
$P_{\min}$/MPa	1.014	1.989	5.014	7.015	12.053	11.029
$P_{\max}$/MPa	25.103	25.055	25.056	25.029	25.054	25.028
$\rho_{\min}$/kg·m^{-3}	678.23	678.97	686.43	693.68	681.16	449.95
$\rho_{\max}$/kg·m^{-3}	734.06	736.20	745.78	762.23	814.17	876.18
data points	148	144	124	111	78	81
c_1/MPa·kg^{-1}·m^3	0.159724	0.154668	0.135714	0.103402	0.021617	−0.004692
c_2/kg^{-1}·m^3	1.195×10^{-3}	1.191×10^{-3}	1.174×10^{-3}	1.152×10^{-3}	1.129×10^{-3}	1.058×10^{-3}
c_3/MPa	−190.319	−202.930	−211.409	−234.490	−346.673	−180.882
c_4/K·MPa	29 515.986	31 299.251	30 770.939	31 843.812	46 306.191	14 652.310
c_5/MPa·K$^{1/3}$	−2707.4836	−2808.8628	−2768.9001	−2797.1328	−3463.6413	−1504.5692
AAD/%[b]	0.0068	0.0057	0.0047	0.0068	0.0646	0.4591
bias/%[c]	-1.72×10^{-6}	-1.09×10^{-6}	-7.64×10^{-7}	-1.55×10^{-6}	-1.46×10^{-4}	-7.53×10^{-3}
SDV/%[d]	1.56×10^{-4}	1.07×10^{-4}	8.34×10^{-5}	1.71×10^{-4}	1.73×10^{-2}	8.33×10^{-1}
RMS/%[e]	0.0087	0.0074	0.0062	0.0088	0.0854	0.6147

[a] $\%\Delta V = 100((V_{\text{exptl}} - V_{\text{calcd}})/V_{\text{exptl}})$. [b] $\text{AAD} = (1/n)\sum_{i=1}^{n}|\%\Delta V_i|$. [c] $\text{bias} = (1/n)\sum_{i=1}^{n}(\%\Delta V_i)$. [d] $\text{SDV} = \sqrt{1/(n-1)\sum_{i=1}^{n}(\%\Delta V_i - \text{bias})^2}$. [e] $\text{RMS} = \sqrt{(1/n)\sum_{i=1}^{n}(\%\Delta V_i)^2}$.

Table 12. Parameters for Equation 4 for Data Reported in Reference 4

	$x_1 = 0.150$	$x_1 = 0.301$	$x_1 = 0.505$	$x_1 = 0.850$
$T_{\min}$/K	310.93	310.92	311.25	312.46
$T_{\max}$/K	403.08	403.08	402.94	402.80
$P_{\min}$/MPa	6.72	6.76	6.93	8.72
$P_{\max}$/MPa	34.68	34.51	30.94	28.03
$\rho_{\min}$/kg·m^{-3}	652.40	650.08	652.80	571.60
$\rho_{\max}$/kg·m^{-3}	749.30	757.80	778.00	836.80
data points	20	20	17	13
c_1/MPa·kg^{-1}·m^3	0.102223	0.094339	0.070276	0.006335
c_2/kg^{-1}·m^3	1.230×10^{-3}	1.211×10^{-3}	1.173×10^{-3}	1.137×10^{-3}
c_3/MPa	−147.053	−135.888	−205.707	−295.456
c_4/K·MPa	21 191.465	17 752.385	26 986.365	38 034.189
c_5/MPa·K$^{1/3}$	−1957.6624	−1771.6752	−2333.1702	−2856.8387
AAD/%	0.0702	0.0697	0.0736	0.2168
bias/%	-1.41×10^{-4}	-1.31×10^{-4}	-1.20×10^{-4}	-1.42×10^{-3}
SDV/%	1.07×10^{-2}	9.65×10^{-3}	7.27×10^{-3}	1.07×10^{-1}
RMS/%	0.0838	0.0809	0.0776	0.2667

to 363) K and pressures up to 25 MPa. Densities of decane at (30 and 40) MPa were predicted successfully using the parameters determined here for the BWRS EoS. Good agreement was found for experimental densities with those calculated with the equation proposed by Lemmon and Span.[14] A simple empirical equation was used successfully to correlate the densities of CO_2 + decane mixtures at constant composition.

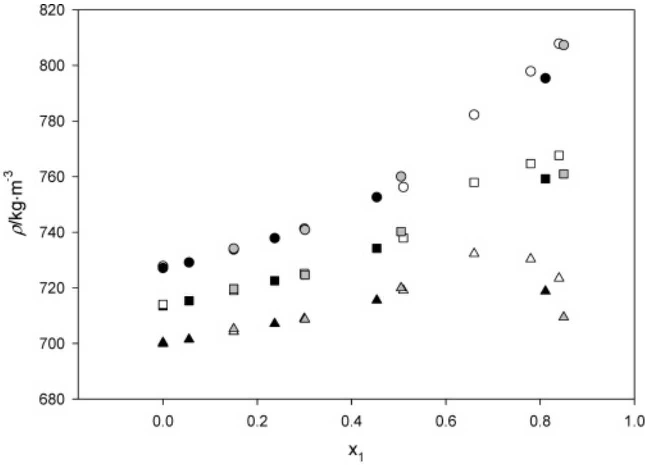

Figure 5. Comparison with data reported by Bessières et al.[5] and Cullick and Mathis[4] at 20 MPa: ●, this work at 318.15 K; ○, Bessières et al.[5] at 318.15 K; shaded ○, Cullick and Mathis[4] at 318.15 K; ■, this work at 338.15 K; □, Bessières et al.[5] at 338.15 K; shaded □, Cullick and Mathis[4] at 338.15 K; ▲, this work at 358.15 K; △, Bessières et al.[5] at 358.15 K; shaded △, Cullick and Mathis[4] at 358.15 K.

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