Temperature and Pressure Dependence of Volumetric Properties for Binary Mixtures of n-heptane and n-octane[†]

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[†]Dedicated to Prof. Dr. Jože Škerjanc on the occasion of his 70th birthday

Abstract

The densities of *n*-heptane, *n*-octane and their binary mixtures were measured at 298.15, 323.15 and 348.15 K and within the pressure range 0.1 to 40 MPa using a vibrating tube densimeter. The reliability of this technique has been verified in our previous works. The partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures were calculated from the obtained densities. This study presents the dependence of densities, partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures on composition, temperature and pressure.

Keywords: Density, partial molar volume, excess molar volume, isothermal compressibility, isobaric thermal expansivity, internal pressure, *n*-heptane, *n*-octane

1. Introduction

n-alkanes form the major components of oil and natural gas. The volumetric properties of *n*-alkanes and their mixtures are of particular interest in connection with the recovery, production and refining of petroleum. Knowledge about the temperature and pressure dependence of volumetric properties for *n*-alkanes is important for the modeling, correlating and developing of petrochemical processes. Although these compounds are widely used, there is still a lack of knowledge about their properties. Whilst there are several publications, some of which will be mentioned here, regarding the properties of *n*-alkanes and their binary and ternary mixtures at atmospheric pressure,[1–8] data regarding properties under high pressures are relatively scarce.[9–14] Only a few researchers have measured the densities of n-heptane, n-octane and their binary mixtures. Data on the experimental densities of *n*-heptane within temperature range 273.15 to 363.15 K and at atmospheric pressure can be found in Ref. 7. Densities at higher pressures were reported for *n*-heptane up to 100 MPa[13] and up to 400 MPa,[9, 11] and n-octane up to 10 MPa.[12] This case study concerns binary mixtures of *n*-heptane and

n-octane in acquiring excess molar volumes at 298.15 K and atmospheric pressure,[4] volumetric properties and viscosities at atmospheric pressure,[1] and pressures up to 10 MPa.[10]

We measured the densities of pure *n*-heptane and *n*-octane and binary mixtures of *n*-heptane and *n*-octane, at 298.15, 323.15 and 348.15 K and within the pressure range 0.1 to 40 MPa, using a vibrating tube densimeter. Furthermore we present the dependence of densities, partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures, on composition, temperature and pressure.

2. Experimental

2. 1. Materials

Carbon dioxide with a purity of 99.995% and nitrogen with a purity of 99.996% were supplied by Messer Slovenija. *n*-heptane with stated purity ≥ 99.5% and *n*-octane with stated purity ≥ 99.5% were obtained from Fluka. Water (purified with Mili-Q Plus system, 18.2 Mcm) and

all of the chemicals were used without further purification and, prior to use, degassed using an ultrasonic bath.

2. 2. Apparatus and Procedures

Densities were determined using a vibrating tube densimeter. Fig. 1 shows a schematic diagram of this apparatus. The main part of the densimeter is an Anton Paar DMA 512 unit with a vibrating U-tube (4), which is connected to a DMA 60 electronic unit (5). The U-tube was thermostated using an external temperature controlled circulating bath, which regulates temperature within $\pm 5 \cdot 10^{-3}$ K (6). The temperature inside the U-tube was measured with an Anton Paar CKT100 platinum resistance thermometer with an uncertainty of 0.01 K. Another thermostat (7) was used for thermostating the interior of the DMA 512 cell. The pressure in the system was regulated by the use of a high pressure Nova Swiss piston pump (3). The pressure was controlled using a Wika pressure gauge. The uncertainty in the pressure measurement is estimated to be 0.05 MPa.

The samples were prepared by weight using an analytical balance with a precision of $\pm 1 \cdot 10^{-7}$ kg and, after ultrasonic degassing, introduced into the measurement system using a syringe. At each temperature and pressure the samples were left in the U-tube until the vibration period was almost constant, so that the system reached thermal equilibrium.

After the measuring procedure, the samples were removed and the measurement system was blown through with nitrogen and pressurized a couple of times with carbon dioxide to more than 20 MPa, so that the rest of the sample was removed.

The reference fluids used were water and nitrogen. The reported uncertainty in the density of water was within 0.001% at temperatures up to 423 K and pressures up to 10 MPa, the uncertainties rose at higher temperatures and pressures, but were generally less than 0.1% in density except under extreme conditions.[16] The uncertainty in density of nitrogen was within 0.02%.[17] Uncertainty in the measured density is estimated to be within 0.7 kg/m^{3}.

3. Results and Discussion

The densities of pure *n*-heptane and *n*-octane and binary mixtures of *n*-heptane and *n*-octane were measured at 298.15, 323.15 and 348.15 K, and within the pressure range 0.1 to 40 MPa.

The comparisons of some results with literature data for pure *n*-heptane and *n*-octane are presented in Table 1. Generally, agreement between experimental and literature data is good.

The experimental values of the densities differ a little from our previously measured densities of *n*-heptane[15] because we used a more precise temperature indicator and, thus, improved temperature control. Moreover, we added thermostating of the exterior part of the measurement system for better temperature stability.

Table 1. Comparison between the experimental and literature values of densities for pure *n*-heptane and *n*-octane

Component	T	p	ρ_{exp}	ρ_{lit}	Reference
	K	MPa	kg/m^3	kg/m^3	
n-heptane	323.15	0.1	657.1	657.4	12
	323.15	20	677.5	677.1	12
	323.15	40	693.7	692.6	12
	298.15	0.1	678.8	679.6	10
n-octane	323.15	0.1	677.4	677.78	11
	323.15	10	687.2	687.51	11
	348.15	0.1	656.3	656.70	11
	348.15	10	668.0	667.96	11

The values of the densities, isothermal compressibilities, isobaric thermal expansivities and internal pressures of pure *n*-heptane and *n*-octane are listed in Tables 2 and 3.

The partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures were calculated from the obtained densities.

Table 4 presents the densities, partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures of binary mixtures of *n*-heptane and *n*-octane.
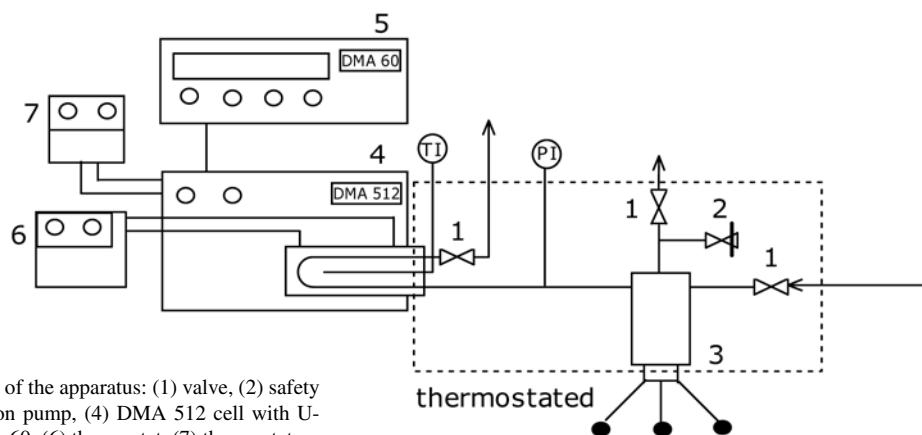

Figure 1. Schematic diagram of the apparatus: (1) valve, (2) safety valve, (3) high pressure piston pump, (4) DMA 512 cell with U-tube, (5) electronic unit DMA 60, (6) thermostat, (7) thermostat.

Table 2. Densities, isothermal compressibilities, isobaric thermal expansivities and internal pressures for pure *n*-heptane

p	ρ	κ_T	a	p_{int}
MPa	kg/m^3	10^4 MPa^{-1}	10^4 K^{-1}	MPa
$T = 298.15$ K				
0.1	678.7	14.25	12.50	261.5
10	687.8	12.64	11.49	261.0
20	696.1	11.26	10.72	263.9
30	703.5	10.11	10.03	265.7
40	710.4	9.18	9.48	268.0
$T = 323.15$ K				
0.1	657.1	17.71	13.42	244.7
10	667.9	15.26	12.00	244.0
20	677.4	13.28	11.00	247.7
30	686.0	11.75	10.16	249.6
40	693.7	10.65	9.51	248.6
$T = 348.15$ K				
0.1	634.7	22.56	14.41	222.3
10	647.8	18.69	12.54	223.6
20	658.8	15.74	11.29	229.7
30	668.7	13.68	10.31	232.3
40	677.4	12.44	9.53	226.8

Table 3. Densities, isothermal compressibilities, isobaric thermal expansivities and internal pressures for pure *n*-octane

p	ρ	κ_T	a	p_{int}
MPa	kg/m^3	10^4 MPa^{-1}	10^4 K^{-1}	MPa
$T = 298.15$ K				
0.1	697.73	12.89	11.46	264.9
10	706.17	11.49	10.69	267.4
20	713.91	10.29	10.07	271.7
30	720.91	9.32	9.41	271.1
40	727.38	8.55	8.95	272.2
$T = 323.15$ K				
0.1	677.38	15.48	12.23	255.2
10	687.20	13.61	11.10	253.5
20	696.01	12.04	10.25	255.0
30	704.02	10.77	9.56	256.9
40	711.25	9.78	8.99	257.2
$T = 348.15$ K				
0.1	656.31	19.47	13.06	233.4
10	668.04	16.43	11.54	234.4
20	678.26	14.08	10.43	238.0
30	687.26	12.38	9.71	243.1
40	695.42	11.32	9.02	237.7

The partial molar volumes were calculated using the following equations:

$$\overline{V}_1 = \frac{1}{\rho}\left(M_1 - V_m \frac{n_2}{(n_1 + n_2)^2} \frac{d\rho}{dx_1} \right) \tag{1}$$

$$\overline{V}_2 = \frac{1}{\rho}\left(M_2 - V_m \frac{n_1}{(n_1 + n_2)^2} \frac{d\rho}{dx_2} \right) \tag{2}$$

where ρ is the density, V_m the volume of the mixture, n_1 number of moles of *n*-heptane, n_2 number of moles of *n*-octane, M_1 the relative molar mass of *n*-heptane, M_2 the relative molar mass of *n*-octane, x_1 is the mole fraction of *n*-heptane and x_2 is the mole fraction of *n*-octane.

Partial molar volumes were calculated by fitting densities regarding a third-degree polynomial to the mole fraction and taking derivatives of densities analytically, with respect to the mole fraction at constant temperature and pressure.

It can be seen from Table 4, that the values for the partial molar volumes of *n*-heptane and *n*-octane increase with rising temperature and decrease with increasing pressure.

The excess molar volumes under certain experimental conditions (temperature and pressure) were calculated from:

$$V^E = \frac{\sum_i x_i M_i}{\rho_m} - \sum_i x_i \frac{M_i}{\rho_i} \tag{3}$$

Table 4. Densities, partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures for binary mixtures of *n*-heptane (1) and *n*-octane (2)

p	ρ	$\overline{V}_1$	$\overline{V}_2$	V^E	κ_T	a	p_{int}
MPa	kg/m^3	cm^3/mol	cm^3/mol	cm^3/mol	10^4 MPa^{-1}	10^4 K^{-1}	MPa
$T = 298.15$ K							
$x_1 = 0.104$							
0.1	696.1	147.2	163.7	−0.0499	12.82	11.69	271.6
10	704.6	145.3	161.8	−0.0277	11.53	10.80	269.4
20	712.3	143.7	160.0	−0.0244	10.38	10.16	271.9
30	719.4	142.2	158.5	−0.0228	9.39	9.51	271.8
40	725.9	140.8	157.0	−0.0203	8.56	9.01	274.1
$x_1 = 0.200$							
0.1	694.6	147.4	163.7	−0.0819	12.88	11.84	273.9
10	703.0	145.5	161.8	−0.0494	11.59	10.90	270.5
20	710.8	143.8	160.0	−0.0454	10.44	10.27	273.3
30	717.9	142.3	158.5	−0.0363	9.45	9.60	272.8
40	724.4	140.9	157.0	−0.0335	8.60	9.09	275.2
$x_1 = 0.300$							
0.1	692.9	147.5	163.6	−0.1025	13.14	11.89	269.6
10	701.5	145.5	161.7	−0.0906	11.71	11.01	270.2
20	709.3	143.8	160.0	−0.0727	10.50	10.27	271.5
30	716.4	142.3	158.4	−0.0692	9.50	9.62	271.8
40	722.9	141.0	157.0	−0.0590	8.71	9.09	271.0
$x_1 = 0.400$							
0.1	691.1	147.5	163.6	−0.1146	13.22	11.95	269.5
10	699.7	145.6	161.7	−0.0938	11.84	11.01	267.4
20	707.6	143.9	159.9	−0.0838	10.62	10.35	270.7
30	714.8	142.4	158.4	−0.0769	9.56	9.68	272.0
40	721.3	141.0	157.0	−0.0628	8.66	9.12	274.1
$x_1 = 0.499$							
0.1	689.2	147.6	163.6	−0.0920	13.44	12.03	266.7
10	697.9	145.7	161.6	−0.0787	11.96	11.14	267.8
20	705.8	143.9	159.9	−0.0665	10.69	10.45	271.5
30	713.0	142.4	158.4	−0.0589	9.64	9.74	271.1
40	719.6	141.0	157.0	−0.0512	8.81	9.21	271.8

p MPa	ρ kg/m³	$\overline{V}_1$ cm³/mol	$\overline{V}_2$ cm³/mol	V^E cm³/mol	κ_T 10⁴ MPa⁻¹	a 10⁴ K⁻¹	p_{int} MPa
$x_1 = 0.596$							
0.1	687.3	147.6	163.5	–0.0826	13.49	12.15	268.4
10	696.0	145.7	161.6	–0.0644	12.07	11.21	266.8
20	704.0	143.9	159.9	–0.0550	10.82	10.52	269.7
30	711.3	142.4	158.3	–0.0545	9.75	9.82	270.2
40	717.9	141.1	156.9	–0.0480	8.85	9.25	271.8
$x_1 = 0.700$							
0.1	685.1	147.6	163.5	–0.0507	13.63	12.20	266.8
10	693.9	145.7	161.6	–0.0395	12.22	11.20	263.2
20	702.0	144.0	159.9	–0.0350	10.96	10.58	267.6
30	709.3	142.4	158.3	–0.0331	9.86	9.87	268.6
40	716.0	141.1	156.9	–0.0291	8.89	9.36	273.9
$x_1 = 0.800$							
0.1	683.0	147.6	163.5	–0.0396	13.79	12.47	269.7
10	691.9	145.7	161.6	–0.0258	12.33	11.38	265.0
20	700.1	144.0	159.9	–0.0249	11.05	10.63	266.8
30	707.4	142.4	158.3	–0.0221	9.93	9.96	268.9
40	714.1	141.1	156.9	–0.0144	8.97	9.38	271.9
$x_1 = 0.899$							
0.1	680.9	147.6	163.5	–0.0202	13.99	12.42	264.6
10	689.9	145.7	161.6	–0.0182	12.49	11.40	262.3
20	698.1	144.0	159.9	–0.0159	11.17	10.70	265.4
30	705.5	142.4	158.3	–0.0097	10.06	9.98	266.0
40	712.3	141.1	156.9	–0.0059	9.12	9.44	268.6
$T = 323.15$ K							
$x_1 = 0.104$							
0.1	675.6	152.2	168.6	–0.0239	15.70	12.35	253.9
10	685.5	149.7	166.2	–0.0227	13.76	11.17	252.4
20	694.4	147.7	164.1	–0.0219	12.14	10.30	254.1
30	702.4	145.8	162.3	–0.0180	10.85	9.60	256.0
40	709.7	144.2	160.6	–0.0184	9.87	9.04	256.0
$x_1 = 0.200$							
0.1	673.8	152.3	168.6	–0.0378	15.92	12.49	253.4
10	683.8	149.8	166.2	–0.0360	13.88	11.27	252.3
20	692.7	147.8	164.1	–0.0286	12.22	10.39	254.6
30	700.8	145.9	162.3	–0.0237	10.94	9.66	255.6
40	708.1	144.3	160.6	–0.0269	10.00	9.08	253.5
$x_1 = 0.300$							
0.1	672.0	152.4	168.6	–0.0661	16.14	12.62	252.5
10	682.1	149.9	166.2	–0.0674	14.06	11.38	251.5
20	691.1	147.8	164.1	–0.0611	12.36	10.47	253.7
30	699.3	146.0	162.2	–0.0592	11.03	9.75	255.7
40	706.6	144.4	160.6	–0.0592	10.05	9.15	254.1
$x_1 = 0.400$							
0.1	670.1	152.4	168.6	–0.0856	16.32	12.74	252.0
10	680.3	150.0	166.1	–0.0813	14.19	11.49	251.6
20	689.4	147.9	164.0	–0.0726	12.46	10.56	253.9
30	697.6	146.0	162.2	–0.0670	11.12	9.81	255.1
40	705.0	144.4	160.5	–0.0674	10.15	9.20	253.0
$x_1 = 0.499$							
0.1	668.1	152.5	168.5	–0.0735	16.44	12.82	252.0
10	678.3	150.0	166.1	–0.0612	14.33	11.55	250.4
20	687.5	147.9	164.0	–0.0512	12.60	10.61	252.3
30	695.7	146.1	162.2	–0.0513	11.23	9.85	253.5
40	703.2	144.4	160.5	–0.0512	10.21	9.24	252.3

p MPa	ρ kg/m³	$\overline{V}_1$ cm³/mol	$\overline{V}_2$ cm³/mol	V^E cm³/mol	κ_T 10⁴ MPa⁻¹	a 10⁴ K⁻¹	p_{int} MPa
$x_1 = 0.596$							
0.1	666.0	152.5	168.5	–0.0608	16.68	12.94	250.6
10	676.4	150.0	166.1	–0.0510	14.49	11.63	249.3
20	685.6	147.9	164.0	–0.0377	12.72	10.70	251.8
30	693.9	146.1	162.2	–0.0416	11.35	9.92	252.5
40	701.4	144.5	160.5	–0.0349	10.37	9.30	249.8
$x_1 = 0.700$							
0.1	663.8	152.5	168.5	–0.0360	16.97	13.09	249.0
10	674.3	150.0	166.1	–0.0345	14.70	11.73	247.9
20	683.5	147.9	164.0	–0.0237	12.85	10.75	250.4
30	691.9	146.1	162.1	–0.0253	11.41	9.97	252.5
40	699.4	144.5	160.5	–0.0197	10.36	9.35	251.7
$x_1 = 0.800$							
0.1	661.6	152.5	168.5	–0.0206	17.40	13.18	244.6
10	672.2	150.0	166.1	–0.0143	14.94	11.80	245.2
20	681.5	147.9	164.0	–0.0133	12.99	10.81	248.9
30	690.0	146.1	162.1	–0.0112	11.52	10.03	251.4
40	697.6	144.5	160.5	–0.0127	10.52	9.39	248.6
$x_1 = 0.899$							
0.1	659.4	152.5	168.5	–0.0125	17.45	13.30	246.2
10	670.1	150.0	166.1	–0.0067	15.06	11.88	245.0
20	679.5	147.9	164.0	–0.0098	13.13	10.90	248.2
30	688.0	146.1	162.2	–0.0056	11.66	10.09	249.8
40	695.6	144.5	160.5	–0.0023	10.61	9.47	248.3
$T = 348.15$ K							
$x_1 = 0.104$							
0.1	654.4	157.6	174.0	–0.0524	19.64	13.06	231.3
10	666.3	154.4	171.0	–0.0391	16.63	11.57	232.2
20	676.6	151.8	168.4	–0.0415	14.24	10.44	235.2
30	685.7	149.6	166.2	–0.0355	12.46	9.70	241.0
40	693.8	147.7	164.3	–0.0209	11.26	9.06	240.2
$x_1 = 0.200$							
0.1	652.5	157.7	174.0	–0.0575	19.97	13.18	229.7
10	664.5	154.5	171.0	–0.0497	16.82	11.66	231.2
20	674.9	151.9	168.4	–0.0449	14.38	10.51	234.5
30	684.0	149.7	166.2	–0.0443	12.61	9.73	238.8
40	692.3	147.8	164.3	–0.0377	11.47	9.07	235.3
$x_1 = 0.300$							
0.1	650.5	157.8	174.0	–0.0634	20.44	13.40	228.2
10	662.6	154.6	171.0	–0.0609	17.05	11.77	230.3
20	673.1	152.0	168.4	–0.0598	14.48	10.67	236.6
30	682.3	149.8	166.2	–0.0542	12.70	9.89	241.2
40	690.6	147.8	164.2	–0.0481	11.65	9.21	235.4
$x_1 = 0.400$							
0.1	648.4	157.8	174.0	–0.0728	20.45	13.59	231.1
10	660.7	154.6	170.9	–0.0668	17.27	11.99	231.8
20	671.2	152.0	168.4	–0.0627	14.75	10.78	234.4
30	680.5	149.8	166.2	–0.0569	12.87	9.94	238.8
40	688.9	147.9	164.2	–0.0535	11.58	9.28	239.0
$x_1 = 0.499$							
0.1	646.3	157.8	174.0	–0.0717	20.89	13.69	228.1
10	658.7	154.7	170.9	–0.0633	17.47	11.98	228.8
20	669.3	152.1	168.3	–0.0603	14.85	10.78	232.9
30	678.7	149.8	166.1	–0.0558	12.98	9.97	237.3
40	687.1	147.9	164.2	–0.0540	11.83	9.26	232.3

p	ρ	$\overline{V}_1$	$\overline{V}_2$	V^E	κ_T	a	p_{int}
MPa	kg/m³	cm³/mol	cm³/mol	cm³/mol	10^4 MPa⁻¹	10^4 K⁻¹	MPa
$x_1 = 0.596$							
0.1	644.2	157.9	173.9	–0.0660	21.14	13.79	227.0
10	656.7	154.7	170.9	–0.0563	17.67	12.08	228.0
20	667.4	152.1	168.3	–0.0550	15.00	10.88	232.5
30	676.8	149.8	166.1	–0.0460	13.12	10.02	236.0
40	685.3	147.9	164.2	–0.0414	11.96	9.34	232.0
$x_1 = 0.700$							
0.1	641.8	157.9	173.9	–0.0600	21.57	14.04	226.5
10	654.5	154.7	170.9	–0.0538	18.04	12.30	227.3
20	665.3	152.1	168.3	–0.0483	15.28	10.93	229.2
30	674.9	149.8	166.1	–0.0481	13.25	10.08	234.9
40	683.3	147.9	164.2	–0.0260	11.90	9.34	233.2
$x_1 = 0.800$							
0.1	639.4	157.9	173.9	–0.0272	21.94	13.95	221.3
10	652.3	154.7	170.8	–0.0282	18.23	12.25	224.0
20	663.2	152.1	168.3	–0.0269	15.38	11.00	228.9
30	672.8	149.9	166.1	–0.0259	13.35	10.10	233.6
40	681.4	147.9	164.2	–0.0177	12.08	9.40	230.9
$x_1 = 0.899$							
0.1	637.1	157.9	173.9	–0.0169	22.32	14.26	222.3
10	650.1	154.7	170.8	–0.0158	18.48	12.40	223.6
20	661.0	152.1	168.3	–0.0135	15.55	11.11	228.7
30	670.8	149.9	166.1	–0.0126	13.49	10.21	233.5
40	679.4	147.9	164.2	–0.0079	12.23	9.50	230.2

where i = 1, 2, ρ_m mixture density, ρ_i the densities of pure *n*-heptane (1) and *n*-octane (2) respectively.

The Redlich-Kister type equation was used for the correlation of experimental values of excess molar volumes:

$$V^E = x_1 x_2 \sum_{i=0}^{n} A_i \left(1 - 2x_2\right)^2 \qquad (4)$$

where A_i are coefficients.

Standard deviations of experimental, and calculated values of excess molar volumes were calculated from:

$$\delta\left(V^E\right) = \left| \frac{\sum_{i=1}^{N} V^E_{exp_i} - V^E_{cal_i}}{N-n} \right| \qquad (5)$$

where $V^E_{exp_i}$ is the experimental value of excess molar volume, $V^E_{cal_i}$ the calculated value of excess molar volume, N the number of experimental points, and n the number of coefficients A_i.

Because small differences in density can contribute to large differences in excess molar volumes, we can observe discrepancies in the obtained excess molar volumes by other authors.[1, 4, 8, 10] From Figs. 2–4, one can

see that the values for excess molar volumes are negative regarding our experimental conditions. The deviation from ideal mixture is relatively small (maximum value of excess molar volume at 298.15 and 0.1 MPa is less than –0.12 cm³/mol), but is larger than by the before-mentioned authors, in some cases the values are even positive.[8] The minima obtained is at $x_1 = 0.4$ similar as in Ref. 10.
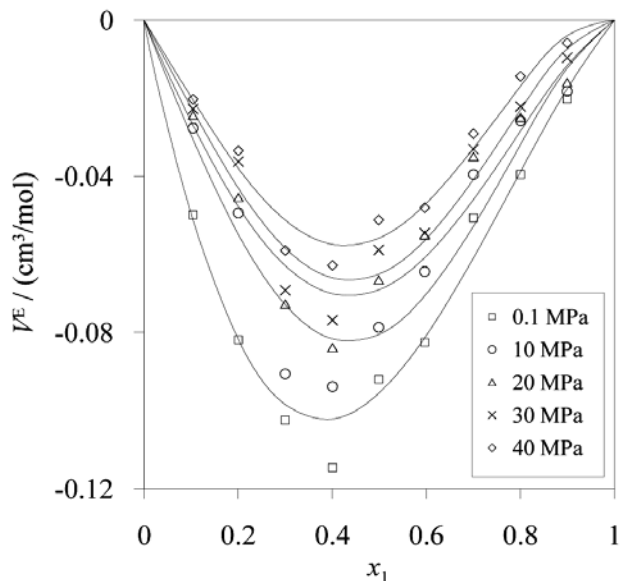
Figure 2. Excess molar volumes as a function of mole fraction at 298.15 K (lines – calculated from Redlich-Kister Eq. 4 with coefficients from Table 5)
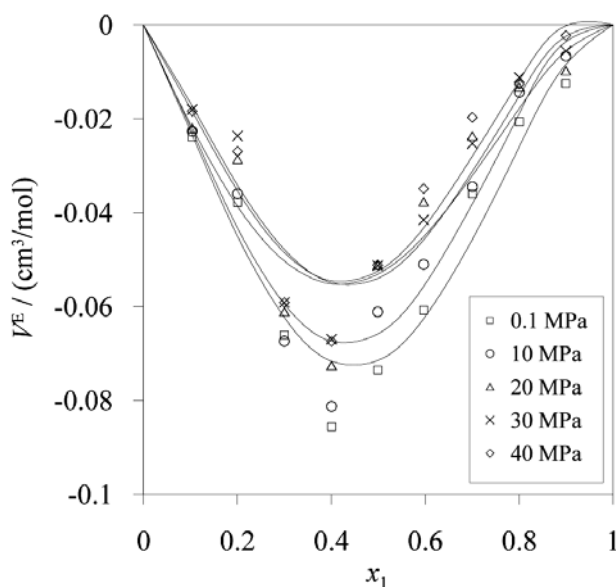
Figure 3. Excess molar volumes as a function of mole fraction at 323.15 K (lines – calculated from Redlich-Kister Eq. 4 with coefficients from Table 5)
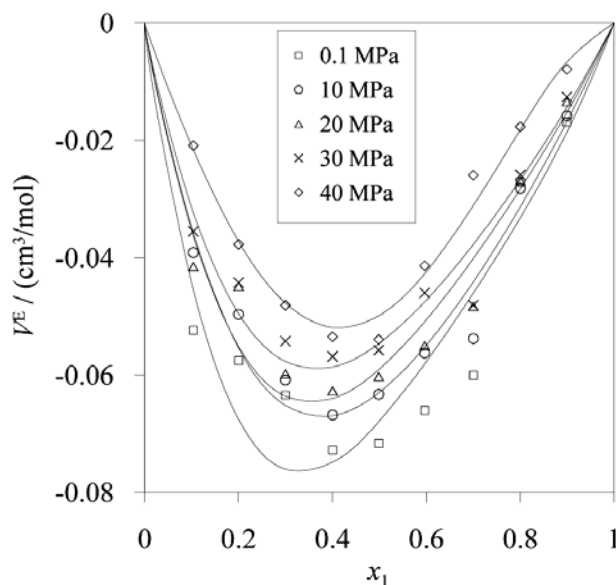
Figure 4. Excess molar volumes as a function of mole fraction at 348.15 K (lines – calculated from Redlich-Kister Eq. 4 with coefficients from Table 5)

Table 5. Coefficients of the Redlich-Kister equation (4) and standard deviations of experimental and calculated values of excess molar volumes

p MPa	A_0 cm³/mol	A_1 cm³/mol	A_2 cm³/mol	$\delta(V^E)$ cm³/mol
T = 298.15 K				
0.1	0.3853	0.2233	0.0138	$4.98 \cdot 10^{-05}$
10	0.3217	0.1196	0.1406	$1.32 \cdot 10^{-04}$
20	0.2761	0.1007	0.1054	$8.18 \cdot 10^{-05}$
30	0.2601	0.1044	0.1493	$6.51 \cdot 10^{-05}$
40	0.2231	0.1096	0.1434	$2.59 \cdot 10^{-05}$
T = 323.15 K				
0.1	0.2858	0.0989	0.1777	$6.80 \cdot 10^{-05}$
10	0.2631	0.1267	0.1915	$6.60 \cdot 10^{-05}$
20	0.2122	0.1083	0.0995	$1.15 \cdot 10^{-04}$
30	0.2159	0.0989	0.1720	$7.84 \cdot 10^{-05}$
40	0.2097	0.1221	0.1724	$8.27 \cdot 10^{-05}$
T = 348.15 K				
0.1	0.2714	0.1786	0.1208	$1.04 \cdot 10^{-04}$
10	0.2518	0.1252	0.0531	$2.80 \cdot 10^{-05}$
20	0.2360	0.1395	0.0687	$3.97 \cdot 10^{-05}$
30	0.2184	0.1187	0.0553	$2.81 \cdot 10^{-05}$
40	0.1994	0.0991	0.0727	$8.29 \cdot 10^{-06}$

The isothermal compressibilities κ_T can be obtained from densities according to:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \qquad (6)$$

where V is the molar volume. The derivatives of a third-degree polynomial of the densities with respect to pressure at constant temperature, were calculated analytically.

It is obvious from Fig. 5 that isothermal compressibilities increase with increasing temperature and decrease with increasing pressure.
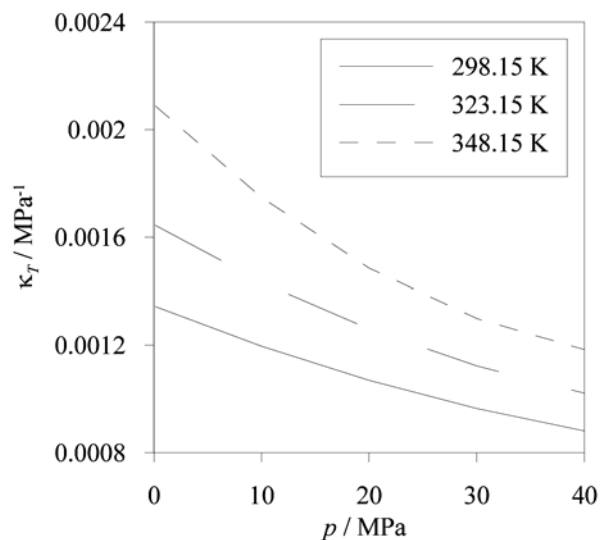

Figure 5. Isothermal compressibilities as a function of pressure (x_1 = 0.499)

The isobaric thermal expansivities were calculated from densities using the following equation:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (7)$$

The derivatives of the densities' quadratic polynomial with respect to temperature at constant pressure were calculated analytically. In Fig. 6 the isobaric thermal expansivities for binary mixture of *n*-heptane and *n*-octane are plotted against pressure. The isobaric thermal expansivities increase with increasing temperature and decrease with increasing pressure.

The obtained values for isothermal compressibilities and isobaric thermal expansivities for *n*-heptane agree within 1.4% and 1.6% with those reported in Ref. 9.

Internal pressures were obtained from:

$$p_{int} = \frac{\alpha T}{\kappa_T} - p \qquad (8)$$

Internal pressures decrease with increasing temperature and increase with increasing pressure (Table 4).

The estimated uncertainties of partial molar volumes, excess molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures are 0.2 cm³/mol, $0.1 \cdot 10^{-3}$ cm³/mol, $0.02 \cdot 10^{-4}$ MPa⁻¹, $0.01 \cdot 10^{-4}$ K⁻¹, 0.6 MPa, respectively.
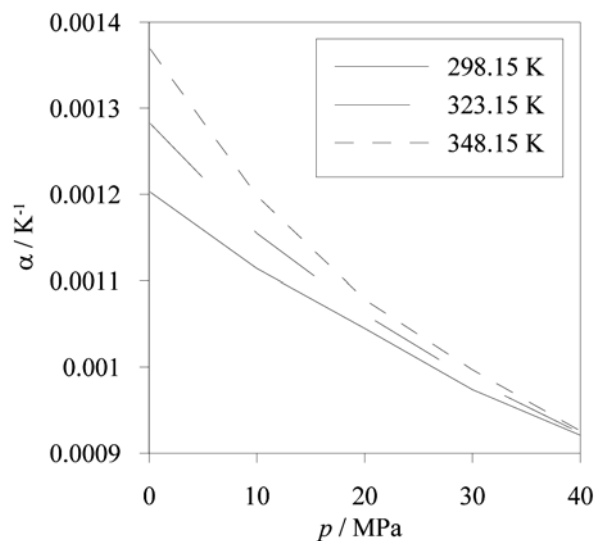
Figure 6. Isobaric thermal expansivities as a function of pressure (x_1 = 0.499)

4. Conclusions

The densities of *n*-heptane, *n*-octane and their binary mixtures were measured at 298.15, 323.15 and 348.15 K and within the pressure range 0.1 to 40 MPa using a vibrating tube densimeter. The properties calculated from the obtained densities were compared with available literature data. The present data for isothermal compressibilities and isobaric thermal expansivities are in good agreement with those already published,[9] while the values of excess molar volumes could not be directly compared, because of different experimental conditions. Generally our values are more negative, so that the difference between our mixtures and ideal mixture is, in our case, bigger than in those published in Refs. 1, 4, 10. For the comparison of partial molar volumes there are, to the best of our knowledge, no available data in literature.

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Povzetek

S pomočjo gostotomera z nihajočo U-cevko smo izmerili gostote heptana, oktana in njunih binarnih mešanic pri 298,15, 323,15 in 348,15 K ter v območju tlakov od 0,1 do 40 MPa. Zanesljivost te tehnike je bila preverjena v naših prejšnjih delih. Iz dobljenih gostot smo izračunali parcialne molske prostornine, presežne molske prostornine, izotermne stisljivosti, prostorninski raztežnostni koeficienti in notranji tlak. Nadalje smo predstavili, kako se gostote, parcialne molske prostornine, presežne molske prostornine, izotermna stisljivost, prostorninski raztežnostni koeficient ter notranji tlak spreminjajo s sestavo, temperaturo in tlakom.