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New Loading Technique for a Vibrating Tube Densimeter and Measurements of Liquid Densities up to 39.5 MPa for Binary and Ternary Mixtures of the Carbon Dioxide–Methanol–Propane System

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Special equipment has been designed and constructed to measure pressure–volume–temperature (PVT) data through the vibrating tube method. At constant temperature, pressure is increased by steps using a pressurizing cell. For each stabilized pressure value, the vibrating frequency of the tube is recorded and translated into density through calibration with known density samples. Experimental PVT measurements on several pure compounds and mixtures have been carried out. Data reliability has been verified by comparisons with literature data available for methane–, ethylene–, methanol–, propane–, 4-methyl-1-pentene–, and *n*-heptane–methylcyclopentane binary mixtures for temperatures between 298 and 398 K and pressures between 2.5 and 39.5 MPa. New data are given for binary and ternary liquid mixtures of the carbon dioxide–methanol–propane system at four temperatures, 323, 348, 373, and 398 K, between 2.5 and 39.5 MPa.

Introduction

The vibrating tube densimeter is widely distributed in laboratories. It is reliable and simple to use. Nevertheless, extension of its application to high-pressure pressure–volume–temperature (PVT) data of pure compounds and mixtures is far from trivial and requires the construction and setup of specific peripherals and development of a reliable experimental method.

In this work, only supercritical fluids and compressed liquids have been investigated.

Experimental Section

Generalities. The apparatus has been designed around the widely used commercial vibrating tube densimeter of Anton Paar, model DMA 512. The measuring cell (*1–3*) is composed of an oscillator (stainless U-tube of 2.4-mm internal diameter) containing 2 cm^3 of liquid. The vibration period, τ, of the U-tube is represented, as a first approximation, by eq 1, where ρ is the density (kg·m^{-3}) of the component inside

$$\tau^2 = (1/K)\rho + B \qquad (1)$$

the U-tube and K and B are characteristic parameters. B is assumed to be temperature- and pressure-independent.

K, which is simultaneously dependent on temperature and pressure (*4*, *5*), is determined by measuring τ for two components whose densities are known over a large range of pressure and temperature. In this work, the chosen two compounds are water (1) and nitrogen (2).

K is given by

$$K(T,P) = (\rho_1 - \rho_2)/(\tau_1^2 - \tau_2^2) \qquad (2)$$

where ρ_1 and ρ_2 are the densities of compounds 1 and 2 under the same conditions of pressure P and temperature T. Discrete $K(T,P)$ values were determined by measurements of τ and the use of literature data for the density of water (*6*, *7*) and nitrogen (*8*). Figures 1 and 2 give examples of $K(T,P)$ values for several temperatures and pressures. Figure 1 shows the temperature influence on K at given pressures while figure 2 shows the pressure influence on K at given temperatures.

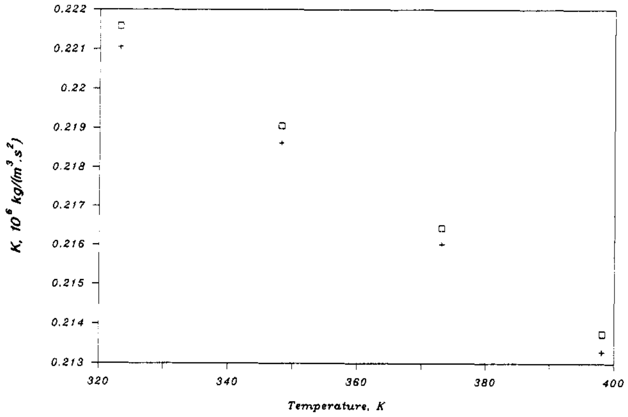

Figure 1. Characteristic parameter, K, of the vibrating tube as a function of temperature at different pressures: (□) P = 5 MPa, (+) P = 22.5 MPa.

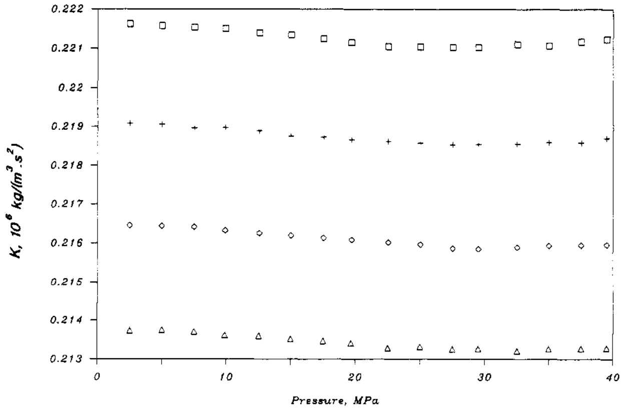

Figure 2. Characteristic parameter, K, of the vibrating tube as a function of pressure at different temperatures: (□) T = 323.20 K, (+) T = 348.20 K, (◇) T = 373.15 K, (△) T = 398.15 K.

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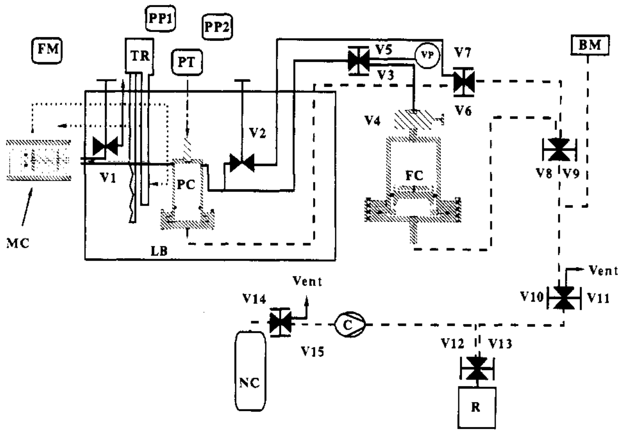

Figure 3. Flow diagram of the apparatus: (BM) Bourdon manometer, (C) compressor, (FC) feed cell, (FM) frequency meter, (LB) liquid bath, (MC) measurement cell, (NC) nitrogen cylinder, (PC) pressure-control cell, (PT) pressure transducer, (PP*i*) platinum probe *i*, (R) reservoir, (TR) thermal regulator, pump, and stirrer, (V_i) shut-off valve *i*, (VP) vacuum pump, (···) circuit for temperature-regulating fluid, (- - -) pressure-control gas (nitrogen) circuit, (—) circuit of fluid under study or calibrating fluid.

Table 1. Molecular weight, Purity, and Origin of Pure Compounds

compound	mol wt	purity type	certified purity (%)	max water content (%)	supplier
n-heptane	100.21	GLC	99.9	0.005	Aldrich
methylcyclopentane	84.16	GLC	99		Fluka
ethylene	28.054	vol	99.95		Air Liquide
4-methyl-1-pentene	84.16	GLC	96		Interchim
methanol	32.042	GLC	99.5	0.01	Merck
propane	44.097	vol	99.95		Air Gaz
CO_2	44.01	vol	99.995		Air Liquide
methane	16.043	vol	99.995		Air Liquide

Table 2. Molar Volume V_m of Methane as a Function of Pressure P at T = 323.15 K

P (MPa)	$V_m{}^a$ (10^{-6} m^3/mol)	$V_m{}^b$ (10^{-6} m^3/mol)	rel dev in molar vol [$(\delta V_m/V_m) \times 100$]^c
10.11	237.72	238.14	0.18
21.03	112.36	112.40	0.01
32.70	80.02	80.08	0.07
38.55	72.60	72.61	0.01

[a] This work. [b] Reference 9. [c] $\delta V_m/V_m = (V_m(\text{this work}) - V_m(\text{ref } 9))/V_m(\text{this work})$.

Table 3. Molar Volume V_m of Ethylene as a Function of Pressure P at T = 373.15 K

P (MPa)	$V_m{}^a$ (10^{-6} m^3/mol)	$V_m{}^b$ (10^{-6} m^3/mol)	rel dev in molar vol [$(\delta V_m/V_m) \times 100$]^c
5.00	532.06	532.50	0.08
7.50	327.79	327.16	0.19

[a] This work. [b] Reference 14. [c] $\delta V_m/V_m = (V_m(\text{this work}) - V_m(\text{ref } 14))/V_m(\text{this work})$.

Knowing the calibration function $K(T,P)$ and the period of vibration, τ, at T and P, the density, ρ, of a sample is given by

$$\rho(T,P) = \rho_1(T,P) + (\tau^2 - \tau_1{}^2)K(T,P) \qquad (3)$$

Table 4. Specific Volume v of Methanol as a Function of Pressure P at T = 373.15 K

P (MPa)	v^a (10^{-3} m^3/kg)	v^b (10^{-3} m^3/kg)	rel dev in specific vol [$(\delta v/v) \times 100$]^c
2.50	1.401	1.4005	−0.04
5.00	1.394	1.3931	−0.07
10.00	1.380	1.3795	−0.04
20.00	1.356	1.3559	−0.01
30.00	1.336	1.3358	−0.01

[a] This work. [b] Reference 15. [c] $\delta v/v = (v(\text{this work}) - v(\text{ref } 15))/V(\text{this work})$.

Apparatus. The flow diagram of the apparatus is given in Figure 3. The measurement cell, MC, containing the vibrating tube is thermoregulated by circulating a liquid pumped from inside the regulating liquid bath, LB. A 100-Ω platinum probe, PP1, gives the temperature inside the vibrating tube. One side of the vibrating tube is closed by the shut-off valve, V_1. The other side is connected to the pressure-control cell, PC, and then to the feed cell, FC. The pressure-control and feed cells contain pistons to separate the fluid under study from the pressure-control gas (nitrogen) introduced at the bottom of the cells. Nitrogen can enter the measuring circuit through valves V_2 and V_7 for pressure transducer calibration purposes. The reservoir, R, contains nitrogen at a pressure much higher than 40 MPa; it is filled through a 110-MPa compressor (Nova Swiss).

Experimental Procedure. Calibrations. First of all, the platinum probes (Specitec) have been calibrated against a 25-Ω reference platinum probe (Lyon-Allemand-Louyot, model STHP-B) connected to a four-way digital multimeter (Enertec-Schlumberger, model 7081). The accuracy is estimated to be 0.02 K.

The pressure transducer (Sedeme, type CMB500) is calibrated at each working temperature against a digital manometer (Heise 0–25 MPa, model 901A, and Heise 0–50 MPa, model 710A). The two digital manometers are calibrated against a dead weight balance (Desgranges et Huot, model 5202). The final accuracy on measured pressures is about 0.05 MPa for pressures between 25 and 50 MPa and 0.03 MPa for pressures below 25 MPa.

Loading of the Measurement Cell. A pure liquid compound, such as water, is first degassed and then distilled under vacuum into the evacuated feed cell.

Loading is more complex for a binary mixture. First the degassed less volatile component is transferred by low-pressure distillation into the weighed (empty) feed cell. Then a new weighing of the feed cell is performed to know the exact amount introduced. Afterward, if it is a liquid, the second component is transferred in the same manner into the feed cell. If it is a gas, at feed conditions, it is introduced into the feed cell under pressure. A third weighing yields a determination of the mass of the second component and therefore the mixture composition. Weighings are all carried out within 10^{-6} kg (maximum contents of the feeding cell 100 cm^3).

Setup and Measurements. The feed cell is connected to the pressure-control cell with valve V_4 closed. Pressure of nitrogen is applied under its piston. For a binary mixture, the pressure applied is much higher than the mixture bubble pressure.

The circuits and cells between valve V_4 and valve V_1 are evacuated using the vacuum pump, VP. Then valve V_5 is closed and valve V_4 slightly opened to introduce enough fluid under study to reach the equilibrium pressure, at the temperature of the regulated liquid bath, LB. Valve V_4 is then closed. The exact required equilibrium pressure is adjusted using the pressure-control gas in the PC. When temperatures measured through PP1 and PP2 are the same within experimental accuracy (see Calibrations) and the pressure is stable, the vibration period of the vibrating tube is recorded and the pressure is increased, through the pressure-control cell, to perform new measurements and so on for a

Table 5. Propane Molar Volume V_m as a Function of Pressure P at Different Temperatures

P (MPa)	$V_m{}^a$ (10^{-6} m^3/mol)	$V_m{}^b$ (10^{-6} m^3/mol)	rel dev in molar vol [$(\delta V_m/V_m) \times 100$]^c
		T = 323.20 K	
2.50	97.34	97.38	−0.05
5.00	94.93	94.99	−0.07
7.50	93.06	93.15	−0.09
9.90	91.63	91.69	−0.07
12.50	90.26	90.35	−0.08
15.00	89.10	89.24	−0.15
17.50	88.06	88.25	−0.22
19.70	87.25	87.46	−0.24
22.50	86.30	86.56	−0.30
25.00	85.60	85.82	−0.25
27.50	84.93	85.14	−0.24
29.50	84.43	84.63	−0.23
32.50	83.75	83.91	−0.20
35.00	83.21	83.36	−0.18
37.50	82.71	82.84	−0.16
39.30	82.34	82.49	−0.18
		T = 348.20 K	
5.00	106.64	106.70	−0.06
7.50	102.45	102.45	−0.00
9.90	99.61	99.63	−0.02
12.50	97.25	97.30	−0.05
15.00	95.39	95.49	−0.10
17.50	93.82	93.97	−0.16
19.70	92.63	92.80	−0.18
22.50	91.30	91.49	−0.21
25.00	90.24	90.45	−0.24
27.50	89.34	89.52	−0.20
29.50	88.67	88.83	−0.18
32.50	87.74	87.88	−0.16
35.00	87.04	87.15	−0.13
37.50	86.42	86.48	−0.07
39.30	85.93	86.02	−0.11
		T = 373.15 K	
5.00	139.87	139.68	0.14
7.50	118.22	118.08	0.12
10.00	110.94	110.94	0.00
12.50	106.53	106.57	−0.04
15.00	103.35	103.42	−0.07
17.50	100.83	100.97	−0.14
20.00	98.79	98.96	−0.17
22.50	97.10	97.26	−0.16
25.00	95.61	95.79	−0.19
27.50	94.32	94.49	−0.18
30.00	93.20	93.34	−0.15
32.50	92.16	92.29	−0.15
35.00	91.23	91.34	−0.12
37.50	90.38	90.47	−0.10
39.50	89.73	89.82	−0.10
		T = 398.15 K	
7.50	157.82	157.67	0.10
10.00	130.24	129.98	0.20
12.50	120.03	119.88	0.13
15.00	114.03	113.94	0.08
17.50	109.82	109.80	0.02
20.00	106.61	106.65	−0.03
22.50	104.07	104.11	−0.04
25.00	101.97	102.00	−0.03
27.50	100.16	100.20	−0.04
30.00	98.57	98.63	−0.06
32.50	97.20	97.24	−0.04
35.00	95.98	95.99	−0.01
37.50	94.87	94.87	−0.00
39.50	94.04	94.04	−0.00

[a] This work. [b] Reference 16. [c] $\delta V_m/V_m = (V_m(\text{this work}) - V_m(\text{ref } 16))/V_m(\text{this work})$.

whole isotherm. Then, the temperature of the liquid bath is modified and study of a new isotherm is started.

The loading of a mixture requires extra care. The piston of the pressure-control cell must be at the top of the cell when valve V_4 is opened in order to minimize partial vaporization of the mixture. Valve V_1 is slightly opened when all circuitry is loaded at high pressure by the mixture, in order to purge the vibrating tube and fill it with the homogeneous liquid mixture. Then valve V_1 is closed, and the pressure under the pressure-control cell piston is released slowly to fill the pressure-control cell with the mixture. Transfer is stopped, when the needed volume of fluid is reached, by closing valve V_4.

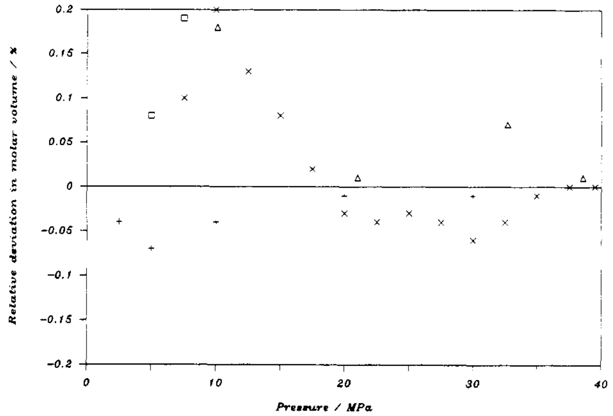

Figure 4. Percent relative deviation of pure component molar volumes ($100\delta V_m/V_m$): (□) ethylene at T = 373.15 K, (+) methanol at T = 373.15 K, (×) propane at T = 398.15 K, (△) methane at T = 325.15 K.

Table 6. Molar Volume V_m of 4-Methyl-1-pentene as a Function of Pressure P at 373.15 K

P (MPa)	$V_m{}^a$ (10^{-6} m^3/mol)	$V_m{}^b$ (10^{-6} m^3/mol)	rel dev in molar vol [$(\delta V_m/V_m) \times 100$]^c
2.50	143.32	143.50	0.13
5.00	141.92	142.10	0.13

[a] Vibrating tube method (VTM). [b] Variable volume cell (VVC) (*10*). [c] $\delta V_m/V_m = (V_m(\text{VTM}) - V_m(\text{VVC}))/V_m(\text{VTM})$.

Table 7. Molar Volume V_m of Methanol as a Function of Pressure P at Four Temperatures

P (MPa)	V_m (10^{-6} m^3/mol)	V_m (10^{-6} m^3/mol)	P (MPa)	V_m (10^{-6} m^3/mol)	V_m (10^{-6} m^3/mol)
	T = 323.20 K	T = 348.20 K		T = 373.15 K	T = 398.15 K
2.50	41.90	43.29	2.50	44.90	46.85
5.00	41.76	43.10	5.00	44.65	46.52
7.50	41.61	42.93	7.50	44.43	46.22
9.90	41.49	42.77	10.00	44.21	45.94
12.50	41.34	42.59	12.50	44.00	45.67
15.00	41.20	42.42	15.00	43.80	45.41
17.50	41.07	42.27	17.50	43.62	45.18
19.70	40.96	42.13	20.00	43.44	44.97
22.50	40.82	41.97	22.50	43.26	44.76
25.00	40.71	41.84	25.00	43.10	44.55
27.50	40.60	41.70	27.50	42.94	44.36
29.50	40.52	41.61	30.00	42.79	44.17
32.50	40.40	41.46	32.50	42.65	44.00
35.00	40.30	41.35	35.00	42.51	43.83
37.50	40.19	41.23	37.50	42.38	43.67
39.30	40.12	41.16	39.50	42.26	43.54

Measurements performed with water and nitrogen are used to calibrate the vibrating tube and obtain K as a function of temperature and pressure. Taking into account all uncertainties and from observation of dispersions of vibrating periods, a cumulative uncertainty of 0.3% in the densities can be estimated.

Results and Discussion

The purity and origin of chemicals used in this work are given in Table 1. Chemicals were used without any purification except for careful degassing.

Table 8. Adjusted Parameters for the BWRS Equation of State[a]

param	propane	methanol
B_0	2.24719504E+01	1.40352677E+01
A_0	1.20116442E+06	1.86465577E+06
C_0	8.54353557E+10	−1.06737629E+11
D_0	3.44251716E+13	−2.71089780E+13
E_0	5.81933613E+15	−1.61310750E+15
b	2.47941323E+03	8.34313992E+02
a	1.29949519E+08	2.38575807E+06
d	−1.27755597E+10	1.08926408E+08
c	1.12999177E+13	7.07342496E+12
α	4.92437878E+04	4.48051368E+04
u	1.92847455E+03	7.03517000E+02

[a] Units used in adjustments are MPa, K, and cm^3/mol. $P = RT/v + (B_0RT - A_0 - C_0/T^2 + D_0/T^3 - E_0/T^4)/v^2 + (bRT - a - d/T)/v^3 + \alpha(a + d/T)/v^6 + c(1 + u/v^2)\exp(-u/v^2)/(v^3T^2)$.

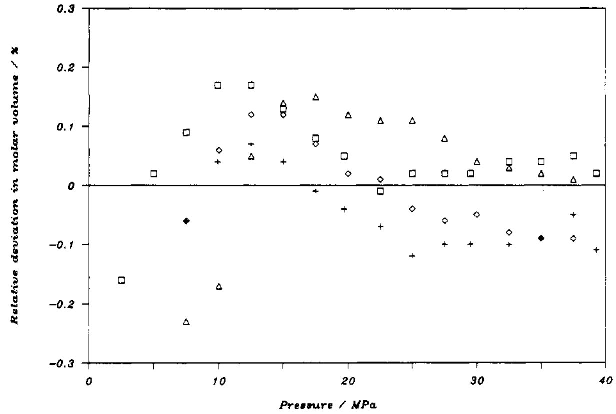

Figure 5. Percent relative deviation of propane molar volumes ($100\delta V_m/V_m$): (□) T = 323.20 K, (+) T = 348.20 K, (◇) T = 373.15 K, (△) T = 398.15 K.

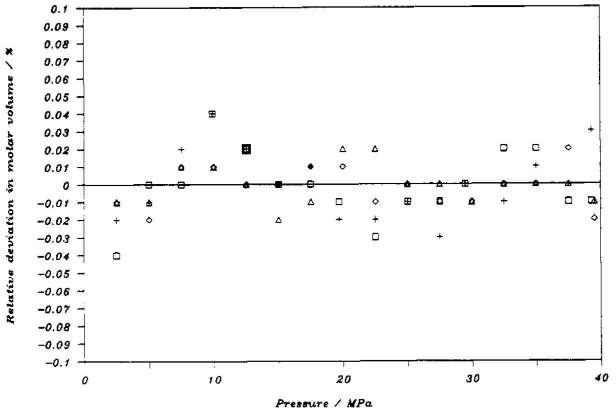

Figure 6. Percent relative deviation of methanol molar volumes ($100\delta V_m/V_m$): (□) T = 323.20 K, (+) T = 348.20 K, (◇) T = 373.15 K, (△) T = 398.15 K.

Several tests were performed to check the reliability of the equipment and data. The molar volume of methane, at 323.15 K, has been determined and compared to literature data (*9*). Good agreement is found (see Table 2); the maximum relative deviation $\delta V_m/V_m$ is 0.18%. Similar agreement is found between literature data and those from this work for ethylene (Table 3), methanol (Table 4), and propane (Table 5). Relative deviations for these four pure component molar volumes are plotted in Figure 4.

The molar volume of 4-methyl-1-pentene has been measured at one temperature and two pressures with the vibrating tube method for comparison with the variable-volume cell technique also developed in the same laboratory (*10*). The absolute average relative deviation between data from the two different sets is 0.13%; see Table 6.

Table 9. Density ρ of the Compressed *n*-Heptane (1)–Methylcyclopentane (2) Liquid System as a Function of Pressure P and *Mole* Fraction $z(1)$ at Four Temperatures

P	ρ (10^3 kg/m^3)				
(MPa)	$z(1)$ = 0.1442	$z(1)$ = 0.4020	$z(1)$ = 0.4663	$z(1)$ = 0.5556	$z(1)$ = 0.6629
T = 298.20 K					
9.90			0.719 10		
19.70			0.727 41		
29.50			0.734 99		
39.30			0.741 11		
T = 323.20 K					
2.50	0.709 72				0.677 01
5.00	0.712 50	0.695 33			0.679 79
7.50	0.715 21				0.682 55
9.90	0.717 99	0.700 52			0.685 22
12.50	0.720 58				0.687 80
15.00	0.723 15	0.705 79			0.690 42
17.50	0.725 43				0.692 79
19.70	0.727 57	0.710 09			0.694 78
22.50	0.730 00				0.697 21
25.00	0.732 29	0.714 96			0.699 58
27.50	0.734 39				0.701 65
29.50	0.735 97	0.718 33			0.703 13
32.50	0.738 45				0.705 56
35.00	0.740 00	0.722 75			0.707 15
37.50	0.742 06				0.709 18
39.30	0.743 30	0.725 63			0.710 27
T = 348.20 K					
2.50	0.685 60				0.654 32
5.00	0.689 08	0.672 98			0.657 87
7.50	0.692 16				0.660 88
9.90	0.695 33	0.679 27	0.676 32	0.669 24	0.664 04
12.50	0.698 57				0.667 25
15.00	0.701 41	0.685 19			0.670 14
17.50	0.704 24				0.672 83
19.70	0.706 68	0.690 31	0.687 88	0.680 78	0.675 28
22.50	0.709 64				0.678 28
25.00	0.712 28	0.695 78			0.680 80
27.50	0.714 61				0.683 13
29.50	0.716 61	0.700 13	0.697 97	0.690 18	0.685 10
32.50	0.719 16				0.687 67
35.00	0.721 44	0.704 77			0.689 75
37.50	0.723 60				0.691 80
39.30	0.724 92	0.708 13	0.706 03	0.698 45	0.693 18
T = 373.15 K					
2.50	0.660 09				0.630 86
5.00	0.664 27				0.635 14
7.50	0.668 47				0.639 00
10.00	0.672 17				0.642 75
12.50	0.675 66				0.646 33
15.00	0.679 16				0.649 72
17.50	0.682 29				0.652 93
20.00	0.685 44				0.656 00
22.50	0.688 46				0.658 95
25.00	0.691 58				0.661 91
27.50	0.694 32				0.664 64
30.00	0.696 88				0.667 28
32.50	0.699 53				0.669 80
35.00	0.701 94				0.672 07
37.50	0.704 33				0.674 53
39.50	0.706 31				0.676 29

Extensive measurements were then performed on methanol at three temperatures (see Table 7). These data and those on propane (Table 5) were correlated with the BWRS equation of state (EOS) (*11*) by least-squares optimization using the following objective function:

$$S = \sum_i [(\rho_{i,\mathrm{exptl}} - \rho_{i,\mathrm{calcd}})/\rho_{i,\mathrm{exptl}}]^2 \qquad (4)$$

Adjusted parameters (these parameters are only valid to represent liquid phases in the defined experimental range and may be correlated) are reported in Table 8. Relative deviations between experimental and calculated values

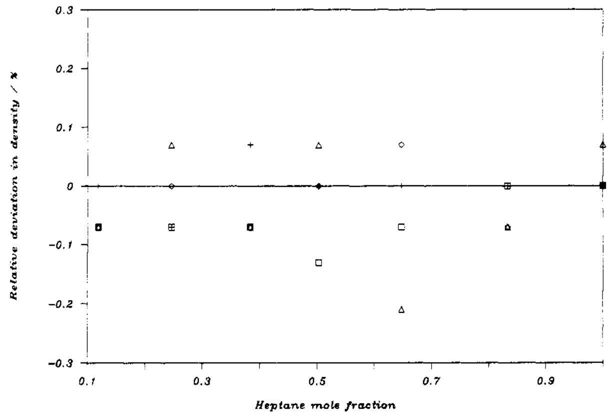

Figure 7. Percent average relative deviation for Osawa et al.'s data of the heptane–methylcyclopentane mixture densities ($100\delta\rho/\rho$) as a function of heptane mole fraction: (□) T = 298.20 K, (+) T = 323.20 K, (◇) T = 348.20 K, (△) T = 373.15 K.

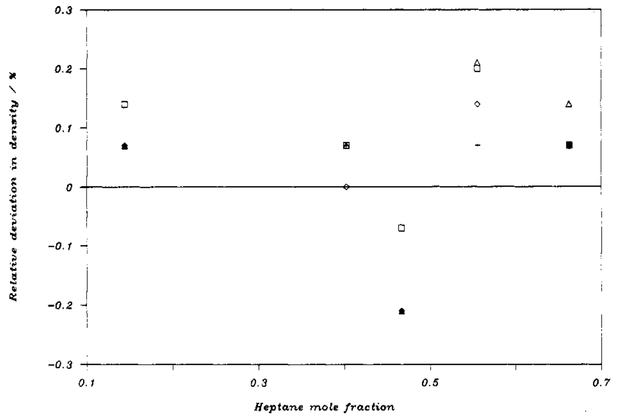

Figure 8. Percent average relative deviation for our data of the heptane–methylcyclopentane mixture densities ($100\delta\rho/\rho$) as a function of heptane mole fraction: (□) T = 298.20 K, (+) T = 323.20 K, (◇) T = 348.20 K, (△) T = 373.15 K.

through the BWRS EOS are plotted in Figures 5 and 6, respectively, for propane and methanol molar volumes as a function of pressure at different temperatures.

Results for the binary mixture n-heptane–methylcyclopentane are reported in Table 9. This mixture was already studied, for different compositions, by Osawa et al. (*12*). Using a polynomial regression of all data (from Osawa et al. and ours) of density as a function of composition and pressure, relative deviations between calculated values and experimental data were obtained and plotted in Figure 7 for Osawa et al.'s data and Figure 8 for ours. Our results appear about 2 times more dispersed than Osawa's.

Table 10 reports new data for the ethylene–4-methyl-1-pentene system.

Table 10. Density ρ of the Liquid Ethylene (1)–4-Methyl-1-pentene Liquid System as a Function of Pressure P and Mole Fraction $z(1)$ at Four Temperatures

	ρ (10^3 kg/m^3)						ρ (10^3 kg/m^3)				
P (MPa)	$z(1)$ = 0.0000	$z(1)$ = 0.2311	$z(1)$ = 0.5392	$z(1)$ = 0.7855	$z(1)$ = 0.9210	P (MPa)	$z(1)$ = 0.0000	$z(1)$ = 0.2311	$z(1)$ = 0.5392	$z(1)$ = 0.7855	$z(1)$ = 0.9210
					T = 323.20 K						
5.00	0.643 45					25.00	0.667 54		0.543 51	0.454 07	0.435 53
7.50	0.646 97		0.489 35			27.50	0.669 88		0.548 02	0.461 86	0.443 15
9.90			0.501 49	0.360 17	0.338 56	29.50			0.551 59	0.467 37	0.448 73
10.00	0.650 33					30.00	0.672 20				
12.50	0.653 46		0.511 37	0.390 25	0.370 42	32.50	0.674 55		0.556 72	0.474 81	0.456 33
15.00	0.656 62		0.519 59	0.409 32	0.390 39	35.00	0.676 71		0.560 46	0.480 64	0.462 05
17.50	0.659 44		0.526 57	0.423 70	0.404 90	37.50	0.678 72		0.563 87	0.485 69	0.467 15
19.70			0.532 25	0.434 21	0.415 58	39.30			0.566 41	0.489 19	0.470 53
20.00	0.662 16					39.50	0.680 37				
22.50	0.664 75		0.538 17	0.445 45	0.426 84						
					T = 348.25 K						
5.00	0.618 78	0.572 97				25.00	0.647 35	0.610 50	0.518 20	0.425 44	0.396 80
7.50	0.622 89	0.578 85	0.436 51			27.50	0.650 17	0.613 76	0.524 33	0.435 16	0.406 83
9.90		0.584 69	0.459 53	0.259 02	0.234 92	29.50		0.616 52	0.528 77	0.442 14	0.414 21
10.00	0.627 04					30.00	0.653 11				
12.50	0.630 80	0.589 60	0.474 79	0.324 15	0.295 71	32.50	0.655 50	0.620 29	0.534 76	0.451 45	0.423 70
15.00	0.634 50	0.594 28	0.486 60	0.359 78	0.330 52	35.00	0.657 97	0.623 32	0.539 64	0.458 29	0.430 75
17.50	0.637 92	0.598 70	0.495 92	0.383 39	0.353 53	37.50	0.660 43	0.626 14	0.543 97	0.464 65	0.437 32
19.70		0.602 30	0.503 37	0.398 83	0.368 97	39.30		0.628 76	0.546 72	0.468 61	0.441 50
20.00	0.641 28					39.50	0.662 37				
22.50	0.644 34	0.606 71	0.511 38	0.413 87	0.384 99						
					T = 373.15 K						
2.50	0.587 22					22.50	0.623 75	0.583 47		0.392 05	0.343 24
5.00	0.593 04	0.540 19				25.00	0.627 31	0.587 76		0.405 64	0.358 47
7.50	0.598 37	0.548 49				27.50	0.630 66	0.591 89		0.417 12	0.371 36
10.00	0.603 28	0.555 80		0.207 36	0.171 20	30.00	0.633 73	0.595 72		0.427 05	0.382 44
12.50	0.607 92	0.562 39		0.276 12	0.225 32	32.50	0.636 63	0.599 33		0.435 68	0.392 06
15.00	0.612 22	0.568 46		0.324 15	0.268 68	35.00	0.639 56	0.602 83		0.443 42	0.400 70
17.50	0.616 31	0.573 72		0.354 04	0.300 39	37.50	0.642 30	0.606 16		0.450 57	0.408 65
20.00	0.620 13	0.578 87		0.375 41	0.324 51	39.50	0.644 42	0.608 50		0.455 70	0.414 22
					T = 398.15 K						
2.50	0.557 39					22.50	0.603 41	0.559 99		0.363 74	0.304 28
5.00	0.565 30	0.502 86				25.00	0.607 70	0.565 15		0.379 82	0.322 46
7.50	0.572 25	0.515 05				27.50	0.611 29	0.570 02		0.392 92	0.337 12
10.00	0.578 65	0.525 21		0.167 23	0.138 28	30.00	0.615 01	0.574 59		0.404 76	0.350 54
12.50	0.584 47	0.533 92		0.229 16	0.182 34	32.50	0.618 22	0.578 74		0.414 61	0.361 93
15.00	0.589 72	0.541 47		0.282 22	0.222 22	35.00	0.621 63	0.582 90		0.423 66	0.372 32
17.50	0.594 77	0.548 40		0.317 99	0.255 88	37.50	0.624 68	0.586 53		0.431 74	0.381 20
20.00	0.599 14	0.554 38		0.343 61	0.282 34	39.50	0.627 03	0.589 43		0.437 53	0.387 73

Table 11. Density ρ of the Carbon Dioxide (1)–Methanol (2) Compressed Liquid Mixture as a Function of Pressure P and Mole Fraction $z(1)$ at Temperature T

	ρ (10^3 kg/m^3)			
P (MPa)	$z(1)$ = 0.0000	$z(1)$ = 0.0961	$z(1)$ = 0.3524	$z(1)$ = 0.7467
T = 323.20 K				
2.50	0.764 66			
5.00	0.767 23			
7.50	0.769 95	0.792 54		
9.90	0.772 25	0.795 62		
12.50	0.775 11	0.799 06	0.824 65	0.786 35
15.00	0.777 68	0.802 22	0.829 87	0.806 60
17.50	0.780 08	0.805 37	0.835 11	0.824 78
19.70	0.782 27	0.807 93	0.839 27	0.838 05
22.50	0.784 84	0.811 24	0.844 38	0.852 12
25.00	0.787 02	0.813 79	0.848 41	0.863 66
27.50	0.789 07	0.816 45	0.852 52	0.873 79
29.50	0.790 80	0.818 56	0.855 61	0.881 25
32.50	0.793 13	0.821 46	0.860 04	0.891 70
35.00	0.795 09	0.823 95	0.863 40	0.899 86
37.50	0.797 15	0.826 38	0.867 32	0.907 35
39.30	0.798 51	0.828 01	0.869 91	0.912 60
T = 348.20 K				
2.50	0.740 11			
5.00	0.743 41			
7.50	0.746 38			
9.90	0.749 14	0.765 96		
12.50	0.752 20	0.770 12	0.779 25	
15.00	0.755 32	0.774 09	0.786 46	
17.50	0.757 98	0.777 51	0.792 96	
19.70	0.760 42	0.780 63	0.798 47	
22.50	0.763 36	0.784 43	0.804 94	
25.00	0.765 78	0.787 61	0.810 20	
27.50	0.768 27	0.790 68	0.815 22	
29.50	0.770 08	0.793 07	0.819 07	
32.50	0.772 70	0.796 52	0.824 52	
35.00	0.774 86	0.799 24	0.828 83	
37.50	0.777 02	0.801 79	0.832 94	
39.30	0.778 43	0.803 62	0.835 82	
T = 373.15 K				
2.50	0.713 64			
5.00	0.717 58			
7.50	0.721 17			
10.00	0.724 66	0.734 16		
12.50	0.728 12	0.739 02	0.726 74	
15.00	0.731 53	0.743 58	0.737 02	
17.50	0.734 58	0.747 93	0.746 26	
20.00	0.737 52	0.752 04	0.754 38	
22.50	0.740 72	0.755 94	0.761 82	
25.00	0.743 41	0.759 72	0.768 71	
27.50	0.746 11	0.763 33	0.775 11	
30.00	0.748 78	0.766 35	0.781 15	
32.50	0.751 25	0.770 08	0.786 60	
35.00	0.753 68	0.773 19	0.792 01	
37.50	0.756 09	0.776 37	0.796 91	
39.50	0.758 10	0.778 80	0.800 78	
T = 398.15 K				
2.50	0.683 90			
5.00	0.688 70			
7.50	0.693 18			
10.00	0.697 40	0.697 69		
12.50	0.701 54	0.703 89		
15.00	0.705 50	0.709 66	0.672 81	
17.50	0.709 10	0.715 04	0.687 81	
20.00	0.712 54	0.720 18	0.700 22	
22.50	0.715 89	0.724 99	0.711 02	
25.00	0.719 18	0.729 39	0.720 75	
27.50	0.722 26	0.733 61	0.729 36	
30.00	0.725 38	0.737 77	0.737 15	
32.50	0.728 17	0.741 54	0.744 38	
35.00	0.730 96	0.745 40	0.751 11	
37.50	0.733 69	0.748 83	0.757 46	
39.50	0.735 82	0.751 63	0.762 18	

Table 12. Density ρ of the Propane (1)–Methanol (2) Compressed Liquid Mixture as a Function of Pressure P and Mole Fraction $z(1)$ at Temperature T

	ρ (10^3 kg/m^3)				
P (MPa)	$z(1)$ = 0.0000	$z(1)$ = 0.0910	$z(1)$ = 0.3482	$z(1)$ = 0.6362	$z(1)$ = 1.0000
T = 323.20 K					
2.50	0.764 66	0.713 14		0.522 85	0.453 02
5.00	0.767 23	0.716 46	0.611 53	0.531 16	0.464 53
7.50	0.769 95	0.719 67	0.616 49	0.538 32	0.473 86
9.90	0.772 25	0.722 44	0.620 80	0.544 27	0.481 24
12.50	0.775 11	0.725 55	0.625 41	0.550 34	0.488 45
15.00	0.777 68	0.728 50	0.629 65	0.555 75	0.494 92
17.50	0.780 08	0.731 56	0.633 63	0.560 80	0.500 76
19.70	0.782 27	0.733 77	0.636 89	0.564 76	0.505 41
22.50	0.784 84	0.736 65	0.640 85	0.569 79	0.510 95
25.00	0.787 02	0.739 16	0.644 07	0.573 60	0.515 13
27.50	0.789 07	0.741 51	0.647 05	0.577 42	0.519 24
29.50	0.790 80	0.743 24	0.649 42	0.579 93	0.522 30
32.50	0.793 13	0.745 94	0.652 74	0.583 87	0.526 53
35.00	0.795 09	0.748 20	0.655 22	0.587 00	0.529 94
37.50	0.797 15	0.750 30	0.658 16	0.590 24	0.533 18
39.30	0.798 51	0.752 06	0.660 12	0.592 28	0.535 53
T = 348.20 K					
2.50	0.740 11	0.685 91			0.056 98
5.00	0.743 41	0.690 17	0.578 66	0.488 65	0.413 53
7.50	0.746 38	0.693 89	0.585 32	0.500 05	0.430 41
9.90	0.749 14	0.697 63	0.591 71	0.509 18	0.442 69
12.50	0.752 20	0.701 40	0.597 17	0.517 56	0.453 43
15.00	0.755 32	0.704 96	0.602 39	0.524 85	0.462 27
17.50	0.757 98	0.708 26	0.607 14	0.531 24	0.470 00
19.70	0.760 42	0.711 02	0.611 22	0.536 44	0.476 05
22.50	0.763 36	0.714 54	0.615 88	0.542 47	0.483 00
25.00	0.765 78	0.717 34	0.619 80	0.547 20	0.488 64
27.50	0.768 27	0.719 77	0.623 57	0.551 67	0.493 58
29.50	0.770 08	0.721 84	0.626 25	0.555 06	0.497 33
32.50	0.772 70	0.724 99	0.630 35	0.559 85	0.502 59
35.00	0.774 86	0.727 43	0.633 41	0.563 45	0.506 64
37.50	0.777 02	0.729 61	0.636 46	0.567 11	0.510 28
39.30	0.778 43	0.731 54	0.638 58	0.569 66	0.513 19
T = 373.15 K					
2.50	0.713 64	0.656 48			0.046 48
5.00	0.717 58	0.661 76	0.538 68	0.427 18	0.315 27
7.50	0.721 17	0.666 36	0.548 87	0.451 46	0.373 02
10.00	0.724 66	0.670 91	0.557 55	0.467 52	0.397 50
12.50	0.728 12	0.675 24	0.565 20	0.479 87	0.413 96
15.00	0.731 53	0.679 35	0.571 88	0.489 91	0.426 67
17.50	0.734 58	0.683 15	0.578 00	0.498 61	0.437 32
20.00	0.737 52	0.686 87	0.583 60	0.506 18	0.446 38
22.50	0.740 72	0.690 36	0.588 87	0.513 09	0.454 14
25.00	0.743 41	0.693 85	0.593 61	0.519 19	0.461 20
27.50	0.746 11	0.697 01	0.598 14	0.524 73	0.467 54
30.00	0.748 78	0.700 07	0.602 19	0.529 83	0.473 13
32.50	0.751 25	0.702 94	0.606 24	0.534 70	0.478 49
35.00	0.753 68	0.705 79	0.609 93	0.539 19	0.483 34
37.50	0.756 09	0.708 50	0.613 48	0.543 42	0.487 93
39.50	0.758 10	0.710 73	0.616 24	0.546 72	0.491 45
T = 398.15 K					
2.50	0.683 90				0.040 30
5.00	0.688 70				
7.50	0.693 18	0.634 62	0.498 91	0.375 25	0.279 42
10.00	0.697 40	0.640 34	0.513 06	0.410 47	0.338 59
12.50	0.701 54	0.645 77	0.524 48	0.431 33	0.367 39
15.00	0.705 50	0.650 79	0.533 98	0.446 68	0.386 72
17.50	0.709 10	0.655 50	0.542 10	0.458 90	0.401 54
20.00	0.712 54	0.659 87	0.549 39	0.469 12	0.413 63
22.50	0.715 89	0.664 04	0.555 98	0.477 91	0.423 74
25.00	0.719 18	0.668 05	0.561 83	0.486 04	0.432 46
27.50	0.722 26	0.671 79	0.567 46	0.493 04	0.440 28
30.00	0.725 38	0.675 30	0.572 32	0.499 45	0.447 35
32.50	0.728 17	0.678 72	0.576 97	0.505 18	0.453 68
35.00	0.730 96	0.682 06	0.581 47	0.510 84	0.459 44
37.50	0.733 69	0.685 24	0.585 68	0.515 66	0.464 82
39.50	0.735 82	0.687 69	0.588 94	0.519 61	0.468 92

Densities as a function of pressure P and temperature T are reported in Tables 11–13 for the three binary systems, respectively, carbon dioxide (1)–methanol (2), propane (1)–methanol (2), and propane (1)–carbon dioxide (2) and in Table 14 for the ternary system propane (1)–methanol (2)–carbon dioxide (3).

Table 13. Density ρ of the Propane (1)–Carbon Dioxide (2) Compressed Liquid Mixture as a Function of Pressure P and Mole Fraction $z(1)$ at Temperature T

	ρ (10^3 kg/m^3)			
P (MPa)	$z(1)$ = 0.6931	$z(1)$ = 0.9167	$z(1)$ = 0.9668	z = 1.0000
		T = 323.20 K		
2.50				0.453 02
5.00		0.469 80	0.466 50	0.464 53
7.50	0.497 11	0.480 86	0.476 61	0.473 86
9.90	0.512 98	0.489 55	0.484 46	0.481 24
12.50	0.526 91	0.497 96	0.492 24	0.488 45
15.00	0.538 16	0.505 25	0.498 92	0.494 92
17.50	0.547 78	0.511 79	0.504 99	0.500 76
19.70	0.555 34	0.517 03	0.509 87	0.505 41
22.50	0.563 80	0.523 09	0.515 57	0.510 95
25.00	0.570 61	0.527 85	0.520 01	0.515 13
27.50	0.576 67	0.532 48	0.524 27	0.519 24
29.50	0.581 34	0.535 65	0.527 44	0.522 30
32.50	0.587 65	0.540 45	0.531 77	0.526 53
35.00	0.592 49	0.544 10	0.535 34	0.529 94
37.50	0.597 57	0.547 79	0.538 79	0.533 18
39.30	0.600 74	0.550 35	0.541 19	0.535 53
		T = 348.20 K		
2.50				0.056 98
5.00		0.406 61	0.409 94	0.413 53
7.50	0.402 58	0.430 54	0.430 56	0.430 41
9.90	0.444 94	0.446 21	0.444 49	0.442 69
12.50	0.470 51	0.459 24	0.456 26	0.453 43
15.00	0.488 02	0.469 73	0.465 82	0.462 27
17.50	0.502 41	0.478 51	0.473 96	0.470 00
19.70	0.512 97	0.485 46	0.480 45	0.476 05
22.50	0.524 53	0.493 23	0.487 70	0.483 00
25.00	0.533 49	0.499 42	0.493 45	0.488 64
27.50	0.541 55	0.505 17	0.498 76	0.493 58
29.50	0.547 38	0.509 38	0.502 68	0.497 33
32.50	0.555 48	0.515 11	0.508 02	0.502 59
35.00	0.561 44	0.519 42	0.512 28	0.506 64
37.50	0.567 34	0.523 84	0.516 23	0.510 28
39.30	0.571 25	0.526 73	0.519 07	0.513 19
		T = 373.15 K		
2.50				0.046 48
5.00				0.315 27
7.50	0.233 17	0.357 13	0.365 01	0.373 02
10.00	0.349 23	0.392 38	0.395 11	0.397 50
12.50	0.400 10	0.413 73	0.413 73	0.413 96
15.00	0.430 08	0.429 34	0.427 79	0.426 67
17.50	0.452 05	0.441 86	0.439 13	0.437 32
20.00	0.468 85	0.452 40	0.448 78	0.446 38
22.50	0.482 75	0.461 42	0.457 10	0.454 14
25.00	0.494 66	0.469 45	0.464 45	0.461 20
27.50	0.505 08	0.476 66	0.471 07	0.467 54
30.00	0.514 07	0.483 12	0.477 04	0.473 13
32.50	0.522 39	0.488 89	0.482 50	0.478 49
35.00	0.529 95	0.494 34	0.487 58	0.483 34
37.50	0.536 87	0.499 32	0.492 54	0.487 93
39.50	0.542 05	0.503 38	0.496 01	0.491 45
		T = 398.15 K		
2.50				0.040 30
7.50		0.236 16		0.279 42
10.00	0.250 68	0.321 79	0.329 27	0.338 59
12.50	0.321 28	0.360 50	0.364 16	0.367 39
15.00	0.366 85	0.384 75	0.386 04	0.386 72
17.50	0.397 73	0.402 63	0.402 17	0.401 54
20.00	0.420 81	0.416 77	0.415 17	0.413 63
22.50	0.439 31	0.428 65	0.426 02	0.423 74
25.00	0.454 50	0.438 77	0.435 37	0.432 46
27.50	0.467 62	0.447 57	0.443 72	0.440 28
30.00	0.478 80	0.455 51	0.450 90	0.447 35
32.50	0.488 76	0.462 65	0.457 50	0.453 68
35.00	0.497 77	0.469 08	0.463 65	0.459 44
37.50	0.505 92	0.475 07	0.469 34	0.464 82
39.50	0.512 18	0.479 65	0.473 54	0.468 92

For propane–carbon dioxide, literature data are available (*13*), but at pressures, temperatures, and compositions different from ours which makes it impossible to perform direct comparisons.

Table 14. Density ρ of the Propane (1)–Methanol (2)–Carbon Dioxide (3) Compressed Liquid Mixture as a Function of Pressure P and Mole Fractions $z(1)$ and $z(2)$ at Temperature T

	ρ (10^3 kg/m^3)			
P (MPa)	$z(1)$ = 0.0534 $z(2)$ = 0.8812	$z(1)$ = 0.2600 $z(2)$ = 0.6558	$z(1)$ = 0.5534 $z(2)$ = 0.2845	$z(1)$ = 0.2001 $z(2)$ = 0.3967
		T = 323.20 K		
2.50		0.644 44		
5.00	0.749 60	0.650 37	0.540 17	
7.50	0.753 07	0.655 88	0.551 59	
9.90	0.755 92	0.660 39	0.560 33	0.664 12
12.50	0.759 21	0.665 37	0.568 96	0.683 33
15.00	0.762 31	0.669 80	0.576 29	0.696 01
17.50	0.765 37	0.674 08	0.582 95	0.706 80
19.70	0.767 76	0.677 64	0.588 31	0.714 98
22.50	0.770 98	0.681 92	0.594 54	0.724 13
25.00	0.773 57	0.685 30	0.599 53	0.731 39
27.50	0.776 06	0.688 66	0.604 25	0.738 06
29.50	0.778 05	0.691 15	0.607 76	0.742 96
32.50	0.780 83	0.694 74	0.612 47	0.749 68
35.00	0.783 20	0.697 46	0.616 49	0.754 97
37.50	0.785 37	0.700 47	0.620 29	0.760 03
39.30	0.787 02	0.702 70	0.623 04	0.763 53
		T = 348.20 K		
5.00	0.721 12	0.613 00		
7.50	0.725 03	0.620 45	0.496 59	
9.90	0.728 91	0.627 43	0.512 39	
12.50	0.733 00	0.633 41	0.525 59	
15.00	0.736 43	0.639 18	0.536 30	
17.50	0.739 86	0.644 29	0.545 37	
19.70	0.742 73	0.648 78	0.552 55	
22.50	0.746 37	0.653 54	0.560 65	
25.00	0.749 56	0.658 09	0.567 20	
27.50	0.752 22	0.662 05	0.573 04	
29.50	0.754 49	0.665 18	0.577 49	
32.50	0.757 85	0.669 45	0.583 60	
35.00	0.760 37	0.672 72	0.588 27	
37.50	0.762 82	0.676 11	0.592 74	
39.30	0.764 83	0.678 41	0.595 87	
		T = 373.15 K		
2.50				
5.00	0.689 64			
7.50	0.694 75	0.561 29		
10.00	0.699 52	0.575 00	0.451 06	
12.50	0.704 17	0.585 34	0.473 39	
15.00	0.708 56	0.594 20	0.489 86	
17.50	0.712 65	0.602 23	0.502 99	
20.00	0.716 52	0.609 21	0.514 07	
22.50	0.720 25	0.615 52	0.523 59	
25.00	0.723 82	0.621 32	0.532 03	
27.50	0.727 24	0.626 66	0.539 66	
30.00	0.730 43	0.631 60	0.546 36	
32.50	0.733 62	0.636 24	0.552 72	
35.00	0.736 52	0.640 65	0.558 42	
37.50	0.739 39	0.644 71	0.563 87	
39.50	0.741 65	0.647 90	0.568 10	
		T = 398.15 K		
5.00	0.653 58			
7.50	0.660 48			
10.00	0.666 73	0.524 79		
12.50	0.672 44	0.541 68	0.407 29	
15.00	0.677 86	0.554 45	0.434 57	
17.50	0.682 89	0.565 08	0.454 57	
20.00	0.687 55	0.574 16	0.470 21	
22.50	0.692 00	0.582 19	0.483 29	
25.00	0.696 17	0.589 28	0.494 25	
27.50	0.700 10	0.595 63	0.503 97	
30.00	0.703 91	0.601 90	0.512 48	
32.50	0.707 55	0.607 40	0.520 24	
35.00	0.710 98	0.612 69	0.527 31	
37.50	0.714 35	0.617 59	0.533 90	
39.50	0.717 05	0.621 60	0.538 88	

Conclusion

This paper reports data on compressed liquid phases, but the method of the vibrating tube densimeter is in the process of being extended for measurements of vapor densities and dew and bubble points of mixtures.

List of Symbols

B	characteristic parameter of the vibrating tube (s^2); see eq 1
$B_0,A_0,C_0,D_0,E_0,b,a,d,c,u$	parameters for the BWRS equation of state (see Table 8)
K	characteristic parameter of the vibrating tube ($\mathrm{kg/m^3 \cdot s^2}$); see eq 1
P	pressure (MPa)
T	temperature (K)
V_m	molar volume ($\mathrm{m^3/mol}$)
v	specific volume ($\mathrm{m^3/kg}$)
z	mole fraction

Greek Letters

δ	uncertainty
ρ	density ($\mathrm{kg/m^3}$)
τ	period (s)

Subscripts

calcd	calculated value
exptl	experimental value
i	compound i

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