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Compressed Liquid Densities and Excess Volumes for the Binary System CO_2 + *N,N*-Dimethylformamide (DMF) from (313 to 363) K and Pressures up to 25 MPa

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Compressed liquid densities for DMF and for CO_2 (1) + DMF (2) binary mixtures are reported from (313 to 363) K and up to 25 MPa. Densities were measured for binary mixtures at nine different compositions, x_1= 0.2618, 0.2876, 0.4068, 0.4268, 0.4461, 0.4502, 0.6235, 0.8091, and 0.9311. There are no experimental density data concerning CO_2 + DMF mixtures reported in the literature. The estimated uncertainty is ±0.20 $kg \cdot m^{-3}$ for the experimental compressed liquid densities. Densities of DMF were correlated with the Benedict−Webb−Rubin−Starling equation of state (BWRS EoS) and the Tait equation. A five-parameter equation was used to correlate the experimental densities of DMF and CO_2 + DMF mixtures. Excess molar volumes were determined using DMF densities calculated from the BWRS EoS and CO_2 densities calculated from the Span−Wagner EoS.

Introduction

New applications for particle formation, materials processing, polymerizations, and these separations using supercritical fluids (SCF) have brought renewed interest to the use of this type of fluid.[1] Phase equilibria and volumetric behavior of mixtures are of great importance to the development of these processes. Supercritical fluid technology strongly depends on the temperature and pressure conditions; consequently, accurate experimental phase equilibria and volumetric properties of SCF + cosolvent binary mixtures are required.[2,3] The addition of a SCF to a polar liquid leads to an enhancement in the fluid properties such as the viscosity, diffusion coefficient, and density,[3] and this effect is important in the antisolvent crystallization process using SCF.[1]

DMF has been used in materials processing in SCF media.[4−6] It is used in the synthesis of pharmaceuticals, in agricultural chemistry, and as a solvent for polymers.[7] DMF is a dipolar aprotic and unassociated solvent.[8,9] It is miscible with almost all common polar and nonpolar solvents.[9]

Phase equilibria and densities of CO_2 + DMF are limited in the literature. Duran-Valencia et al.[10] measured vapor−liquid equilibria for this system. Chang et al.[11] measured solubilities of CO_2 in DMF. Experimental density data were not found in the literature for this binary system. In this paper, experimental compressed liquid densities are reported for DMF and CO_2 + DMF mixtures from (313 to 363) K at pressures up to 25 MPa using a vibrating tube densimeter. Densities of DMF were correlated using the BWRS EoS[12] and the Tait equation.[13] A simple five-parameter empirical equation[14] was used to correlate the densities of DMF and CO_2 + DMF mixtures at fixed compositions.

Experimental Section

Materials. CO_2 and nitrogen were supplied by Infra Air Products México with a certified mol fraction purity of 99.995%. Aldrich supplied HPLC-grade water with a specified mol fraction purity of 99.95%. Merck supplied spectroscopy-grade DMF with a specified mol fraction purity of 99.9%. All compounds were used as received, and no further purification was performed except for a careful degassing under vacuum of water and DMF.

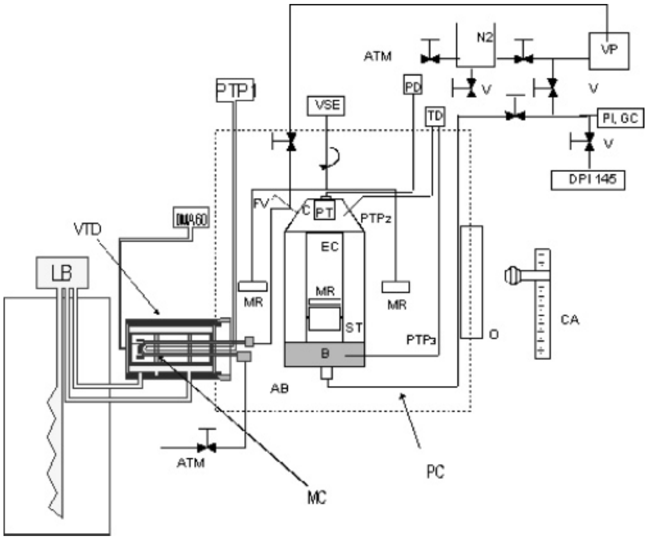

Figure 1. Flow diagram of the apparatus: AB, air bath; CA, cathetometer; DMA 60, period meter; DPI 145, digital indicator of pressure; EC, equilibrium cell; GC, gas compressor; LB, liquid bath; MC, measurement cell; MR, magnetic rod; PI, Isco pump; PT, pressure transducer; PTP*i*, platinum probe *i*;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

Apparatus and Procedure. An Anton Paar DMA 60/512P vibrating tube densimeter (VTD) was used to determine the density. The full scale in temperature is from (263.15 to 423.15) K and in pressure is from (0 to 70) MPa. The manufacturer specifications of the resolution, repeatability, and uncertainty of the density are 1×10^{-6}, 1×10^{-5}, and 1×10^{-4} $g \cdot cm^{-3}$. The VTD requires the building

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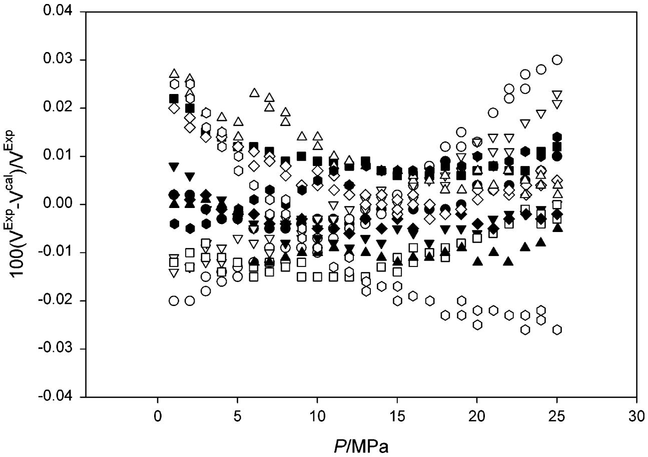

Figure 2. Relative deviations between experimental data and those calculated with eq 5 and the BWRS EoS, with parameters fitted to data reported in this work for DMF at the following temperatures: ●, 313.12 K; ▼, 323.06 K; ■, 333.00 K; ◆, 342.86; ▲, 352.80 K; ●, 362.67 K. Closed and open symbols are for eq 5 and the BWRS EoS, respectively.

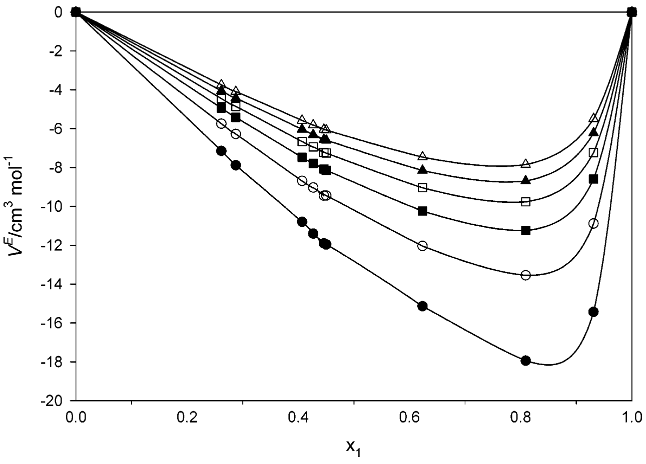

Figure 3. Excess molar volumes of the CO_2 (1) + DMF (2) binary mixtures at ~313.15 K reported in this work: ●, 10 MPa; ○, 11 MPa; ■, 12 MPa; □, 13 MPa; ▲, 14 MPa; △, 15 MPa; −, trend.

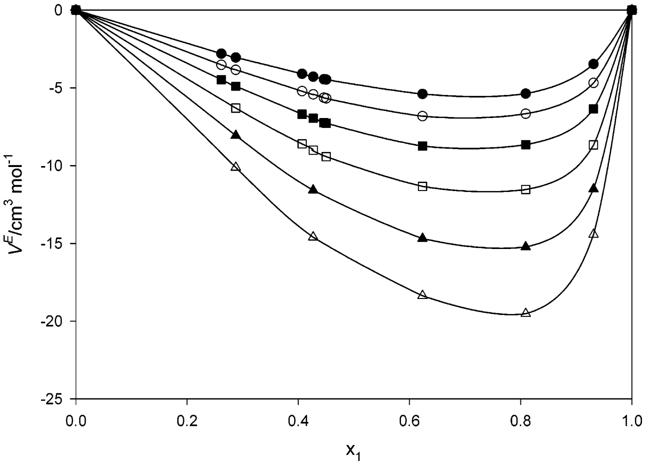

Figure 4. Excess molar volumes of the CO_2 (1) + DMF (2) binary mixtures at ~20 MPa reported in this work: ●, 313.15 K; ○, 323.09 K; ■, 332.99 K; □, 342.92 K; ▲, 352.85 K; △, 362.74 K; −, trend.

and setup of special peripherals. In our case, it was built to determine densities from (313 to 363 K) and pressures up to 25 MPa. Details of the apparatus and experimental procedure used in this work have been described previously.[15−18] The reliability of the experimental density determinations and of the apparatus has been demonstrated in previous papers.[15−17] The experimental apparatus is presented in Figure 1. The measurement circuit consists of the vibrating tube (Hastelloy C-276 U-tube) containing a sample of approximately 1 cm^3. It is connected to a sapphire tube cell, which is used to feed the fluids to the VTD. The experimental procedure is detailed by Zúñiga-Moreno and Galicia-Luna.[16]

Temperature calibrations are made using a calibration system (Automatic Systems F300S) using a 25-Ω reference probe (Rosemount, England, model 162CE; ±0.005 K certified accuracy on the ITS-90 scale) and a water triple-point cell. The uncertainty in the temperature measurements made with a platinum probe Pt 100 is estimated to be ±0.03 K. The pressure measurements are made directly in the equilibrium cell by means of a 25-MPa Sedeme pressure transducer, and their estimated uncertainty is ±0.008 MPa. It was calibrated at temperatures from (313 to 363) K against a dead weight balance (Desgranges & Huot, France, model 5304; accuracy ±0.005% full scale). Water and nitrogen were used as the reference fluids as described in the classical method.[18] The equations of state proposed by Wagner and Pruss[19] and Span et al.[20] were used to calculate the densities of water and of nitrogen, respectively. Calibrating procedures of the platinum temperature probes, the pressure transducer, and the VTD are described in previous papers.[15,21] The estimated uncertainty of the experimental liquid densities presented in this work is ±0.20 kg·m^{-3}. The calculation of the uncertainty of the experimental densities was made according to the next procedure. The vibration period, τ, for nitrogen, water, and DMF is recorded under the same conditions of pressure and temperature within experimental uncertainty, which means that the temperature is fixed and the vibration period is determined at each pressure for all fluids. For a VTD, the density of the studied fluid ρ_F is given by[18]

$$\rho_F = \rho_{H_2O} + K(\tau_F^2 - \tau_{H_2O}^2) \tag{1}$$

where the constant K is expressed in terms of the two reference fluids by

$$K = \frac{\rho_{H_2O} - \rho_{N_2}}{\tau_{H_2O}^2 - \tau_{N_2}^2} \tag{2}$$

On the basis of the propagation of uncertainties, the standard uncertainty in the density σ_{ρ_F} is defined by

$$\sigma_{\rho_F}^2 = \sum_{i=1}^{N}\left(\frac{\partial \rho_F}{\partial X_i}\right)^2 \sigma_{X_i}^2 \tag{3}$$

where the X_i's are referred to as sensitivity coefficients and σ_{X_i} is the standard uncertainty associated with each X_i. Because the density is determined at a fixed temperature and pressure, it is a function only of the water density (ρ_{H_2O}), nitrogen density (ρ_{N_2}), water period (τ_{H_2O}), nitrogen period (τ_{N_2}), and studied fluid period (τ_F). Therefore, the standard uncertainty for the experimental densities is expressed by

$$\sigma_{\rho_F}^2 = \left(\frac{\partial \rho_F}{\partial \rho_{H_2O}}\right)^2 \sigma_{\rho H_2O}^2 + \left(\frac{\partial \rho_F}{\partial \rho_{N_2}}\right)^2 \sigma_{\rho N_2}^2 + \left(\frac{\partial \rho_F}{\partial \tau_{H_2O}}\right)^2 \sigma_{\tau_{H2O}}^2 + \left(\frac{\partial \rho_F}{\partial \tau_{N_2}}\right)^2 \sigma_{\tau_{N2}}^2 + \left(\frac{\partial \rho_F}{\partial \tau_F}\right)^2 \sigma_{\tau_F}^2 \tag{4}$$

Table 1. Experimental Densities of DMF at Six Temperatures

T/K = 313.12		T/K = 323.06		T/K = 333.00		T/K = 342.86		T/K = 352.80		T/K = 362.67	
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}
1.008	930.41	1.014	920.89	1.008	911.34	1.028	901.52	1.040	891.76	1.058	882.04
2.010	931.09	2.007	921.59	2.018	912.08	2.020	902.30	2.009	892.57	2.038	882.89
3.012	931.73	3.026	922.27	3.006	912.78	3.015	903.09	3.011	893.41	3.044	883.77
4.008	932.38	4.006	922.95	4.005	913.51	4.002	903.84	4.020	894.22	4.027	884.62
5.004	933.04	5.016	923.62	5.005	914.23	5.035	904.63	5.050	895.06	5.068	885.54
6.002	933.68	6.010	924.30	6.008	914.97	6.026	905.39	6.060	895.78	6.036	886.37
7.002	934.32	7.006	924.99	7.003	915.68	7.013	906.13	6.996	896.53	7.025	887.22
8.004	934.97	8.010	925.64	8.009	916.39	8.017	906.89	8.008	897.34	8.027	888.03
9.000	935.62	9.012	926.32	9.010	917.11	9.024	907.66	9.034	898.16	9.045	888.90
10.004	936.27	10.014	926.99	10.008	917.81	10.012	908.38	10.019	898.93	10.021	889.71
11.004	936.89	11.011	927.65	11.008	918.51	11.048	909.14	11.043	899.73	11.024	890.55
12.004	937.51	12.013	928.31	12.008	919.20	11.999	909.83	11.998	900.45	11.996	891.30
13.005	938.14	13.007	928.97	13.013	919.90	13.018	910.60	13.028	901.24	13.061	892.19
14.007	938.78	14.011	929.62	14.006	920.57	14.029	911.32	14.015	901.99	14.027	892.95
15.002	939.37	15.008	930.29	15.007	921.24	15.007	912.03	15.028	902.74	15.025	893.73
16.012	940.00	16.014	930.92	16.011	921.92	15.994	912.71	16.000	903.48	15.987	894.49
17.009	940.59	17.004	931.54	17.019	922.59	17.041	913.47	17.011	904.23	17.050	895.32
18.015	941.19	18.006	932.19	18.010	923.27	18.012	914.16	17.999	904.96	18.009	896.08
19.010	941.79	19.006	932.82	19.004	923.91	19.006	914.85	19.044	905.73	19.041	896.85
20.013	942.42	20.005	933.44	20.012	924.58	20.042	915.55	20.050	906.43	20.032	897.62
21.009	942.99	21.002	934.07	21.005	925.24	21.025	916.22	21.038	907.16	21.035	898.36
22.011	943.58	22.013	934.70	22.005	925.88	22.008	916.90	21.955	907.80	22.014	899.10
23.019	944.17	23.015	935.31	23.014	926.52	23.079	917.63	23.009	908.57	23.018	899.87
24.013	944.75	24.008	935.92	24.009	927.19	24.008	918.25	23.996	909.27	24.007	900.58
25.011	945.35	25.012	936.53	25.009	927.83	25.017	918.93	25.056	910.04	25.016	901.35

Table 2. BWRS EOS Adjusted Parameters for DMF

BWRS parameters	DMF
T_{min}/K	313.12
T_{max}/K	362.67
P_{min}/MPa	1.008
P_{max}/MPa	25.056
B_0/cm^3·mol^{-1}	479.78
A_0/bar·cm^6·mol^{-2}	3.7073×10^{7}
C_0/bar·K^2·cm^6·mol^{-2}	-3.0291×10^{11}
D_0/bar·K^3·cm^6·mol^{-2}	1.710386×10^{14}
E_0/bar·K^4·cm^6·mol^{-2}	1.573066×10^{16}
b/cm^6·mol^{-2}	18 645.374
a/bar·cm^9·mol^{-3}	6.90669×10^{7}
d/bar·K·cm^9·mol^{-3}	3.38876×10^{9}
c/bar·K^2·cm^9·mol^{-3}	-1.05572×10^{14}
α/cm^9·mol^{-3}	1.13193×10^{7}
u/cm^6·mol^{-2}	1571.8772
AAD/%	0.0075
bias/%	−0.0004
SDV/%	0.0097
RMS/%	0.0090

Table 3. Tait and Rackett Equations: Adjusted Parameters for DMF

	DMF
T_{min}/K	313.12
T_{max}/K	362.67
P_{min}/MPa	1.008
P_{max}/MPa	25.056
C	-1.03931×10^{6}
b_0/MPa	-2.49997×10^{9}
b_1/MPa	3.00581×10^{8}
E/K	100
A_{R}/kg·m^{-3}	1.69494
B_{R}	3.68341×10^{-2}
C_{R}/K	1.43644×10^{3}
D_{R}	3.80646×10^{-1}
AAD/%	0.0488
bias/%	−0.0135
SDV/%	0.0209
RMS/%	0.0690

where each term is obtained by differentiation of eq 1, resulting in the following expressions

$$\left(\frac{\partial \rho_{\mathrm{F}}}{\partial \rho_{\mathrm{H_2O}}}\right)^2 \sigma^2_{\rho_{\mathrm{H2O}}} = \left[1 + \frac{\tau_{\mathrm{F}}^2 - \tau_{\mathrm{H_2O}}^2}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right]^2 \sigma^2_{\rho_{\mathrm{H2O}}} \tag{5}$$

$$\left(\frac{\partial \rho_{\mathrm{F}}}{\partial \rho_{\mathrm{N_2}}}\right)^2 \sigma^2_{\rho_{\mathrm{N2}}} = \left[-\frac{\tau_{\mathrm{F}}^2 - \tau_{\mathrm{H_2O}}^2}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right]^2 \sigma^2_{\rho_{\mathrm{N2}}} \tag{6}$$

$$\left(\frac{\partial \rho_{\mathrm{F}}}{\partial \tau_{\mathrm{H_2O}}}\right)^2 \sigma^2_{\tau_{\mathrm{H2O}}} = (-2\tau_{\mathrm{H_2O}})^2 \left(\frac{\rho_{\mathrm{H_2O}} - \rho_{\mathrm{N_2}}}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right)^2 \left[\frac{\tau_{\mathrm{F}}^2 - \tau_{\mathrm{N_2}}^2}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right]^2 \sigma^2_{\tau_{\mathrm{H2O}}} \tag{7}$$

$$\left(\frac{\partial \rho_{\mathrm{F}}}{\partial \tau_{\mathrm{N_2}}}\right)^2 \sigma^2_{\tau_{\mathrm{N2}}} = (2\tau_{\mathrm{N_2}})^2 \left(\frac{\rho_{\mathrm{H_2O}} - \rho_{\mathrm{N_2}}}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right)^2 \left[\frac{\tau_{\mathrm{F}}^2 - \tau_{\mathrm{H_2O}}^2}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right]^2 \sigma^2_{\tau_{\mathrm{N2}}} \tag{8}$$

$$\left(\frac{\partial \rho_{\mathrm{F}}}{\partial \tau_{\mathrm{F}}}\right)^2 \sigma^2_{\tau_{\mathrm{F}}} = (2\tau_{\mathrm{F}})^2 \left[\frac{\rho_{\mathrm{H_2O}} - \rho_{\mathrm{N_2}}}{\tau_{\mathrm{H_2O}}^2 - \tau_{\mathrm{N_2}}^2}\right]^2 \sigma^2_{\tau_{\mathrm{F}}} \tag{9}$$

Table 4. Experimental[8] and Calculated Densities of DMF

T/K	ρ^{exptl}/kg·m^{-3}	ρ^{calcd}/kg·m^{-3}	$\dfrac{100(\rho^{\mathrm{exptl}} - \rho^{\mathrm{calcd}})}{\rho^{\mathrm{exptl}}}$
278.15	961.49	962.7	−0.13
283.15	956.98	958.3	−0.14
288.15	952.36	953.8	−0.15
293.15	948.05	949.2	−0.12
298.15	942.92	944.6	−0.18
303.15	938.88	939.9	−0.11
308.15	933.96	935.1	−0.12
313.15	929.55	930.4	−0.09
318.15	925.02	925.6	−0.06
323.15		920.7	
328.15		915.9	
333.15		911.0	
338.15		906.1	
343.15		901.2	
348.15		896.3	
353.15		891.4	
358.15		886.5	
363.15		881.6	
373.15		871.8	

Table 5. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}
				$x_1 = 0.2618$				
	T/K = 313.16			T/K = 323.10			T/K = 333.00	
3.057	946.31	−180.10	3.091	934.49	−187.08			
4.042	947.22	−124.52	4.015	935.38	−133.87	4.056	923.54	−139.74
4.997	948.10	−90.80	4.980	936.31	−98.95	5.026	924.48	−104.54
5.993	948.97	−66.15	5.955	937.21	−74.65	6.035	925.50	−79.66
7.023	949.87	−46.62	7.001	938.19	−55.48	6.980	926.45	−62.56
8.024	950.72	−29.91	7.997	939.10	−41.14	8.017	927.45	−48.11
8.999	951.54	−12.62	9.038	940.05	−28.55	9.008	928.39	−37.08
10.030	952.40	−7.15	10.044	940.96	−18.14	10.028	929.41	−27.74
11.014	953.24	−5.75	11.007	941.80	−11.48	11.020	930.36	−20.32
12.053	954.09	−4.95	12.038	942.72	−8.27	12.076	931.36	−14.47
12.988	954.86	−4.46	13.004	943.54	−6.78	13.005	932.20	−11.13
14.015	955.71	−4.06	14.021	944.43	−5.82	13.999	933.12	−8.92
15.002	956.51	−3.75	14.999	945.30	−5.19	15.008	934.06	−7.49
16.013	957.33	−3.50	16.028	946.18	−4.70	16.020	934.97	−6.52
16.992	958.09	−3.29	16.993	947.00	−4.33	17.005	935.86	−5.83
18.031	958.92	−3.10	18.010	947.83	−4.01	18.041	936.77	−5.27
19.040	959.71	−2.94	19.004	948.68	−3.75	18.979	937.63	−4.86
19.999	960.46	−2.80	20.020	949.52	−3.53	20.048	938.54	−4.48
21.010	961.25	−2.67	21.005	950.32	−3.33	20.998	939.38	−4.20
22.014	962.01	−2.56	22.035	951.15	−3.16	22.045	940.26	−3.93
23.013	962.76	−2.45	23.013	951.94	−3.01	23.012	941.11	−3.71
24.023	963.52	−2.35	24.055	952.80	−2.87	23.999	941.95	−3.52
25.025	964.27	−2.27	25.019	953.55	−2.75	25.038	942.83	−3.34

Table 6. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}
				$x_1 = 0.2876$				
	T/K = 313.15			T/K = 323.09			T/K = 332.99	
4.032	948.43	−137.19						
5.041	949.39	−98.27	5.022	937.32	−107.28			
6.004	950.24	−72.36	6.019	938.29	−80.47	6.007	926.13	−88.06
6.967	951.12	−52.23	7.007	939.23	−60.79	6.998	927.15	−68.34
8.002	952.05	−33.21	8.008	940.16	−44.98	7.991	928.18	−53.15
9.005	952.94	−13.73	9.023	941.14	−31.50	9.021	929.22	−40.53
10.000	953.81	−7.89	10.001	942.04	−20.31	10.024	930.23	−30.45
11.017	954.68	−6.28	11.006	942.98	−12.58	11.006	931.19	−22.37
12.024	955.56	−5.42	12.003	943.90	−9.13	12.020	932.19	−16.12
13.007	956.41	−4.86	13.004	944.81	−7.42	13.024	933.16	−12.12
14.004	957.26	−4.43	14.005	945.73	−6.38	14.028	934.12	−9.70
15.006	958.10	−4.09	14.999	946.61	−5.67	15.010	935.07	−8.19
15.999	958.91	−3.82	15.994	947.48	−5.14	16.010	936.01	−7.13
17.005	959.75	−3.58	17.022	948.41	−4.71	17.003	936.96	−6.37
18.009	960.57	−3.38	17.996	949.25	−4.38	18.005	937.87	−5.77
19.021	961.39	−3.20	19.004	950.13	−4.10	19.008	938.78	−5.29
20.001	962.21	−3.05	20.021	950.99	−3.85	20.007	939.69	−4.90
21.004	963.00	−2.91	21.018	951.84	−3.64	21.004	940.60	−4.58
22.022	963.82	−2.79	22.030	952.68	−3.45	21.990	941.48	−4.30
23.016	964.58	−2.67	23.007	953.51	−3.28	23.037	942.42	−4.04
23.989	965.35	−2.57	24.019	954.35	−3.13	24.000	943.28	−3.84
25.004	966.15	−2.47	25.012	955.16	−3.00	24.996	944.13	−3.64
	T/K = 342.93			T/K = 352.87			T/K = 362.75	
7.012	914.85	−74.56	7.031	902.49	−80.05			
7.999	915.95	−59.52	8.016	903.63	−64.96	8.032	891.20	−69.82
9.007	917.04	−47.40	9.024	904.79	−52.85	9.018	892.47	−57.84
10.005	918.13	−37.72	10.027	905.96	−43.20	9.986	893.65	−48.40
11.003	919.16	−29.78	11.011	907.05	−35.46	10.994	894.89	−40.37
12.011	920.23	−23.28	12.022	908.20	−28.92	12.000	896.09	−33.77
13.016	921.27	−18.22	13.022	909.31	−23.65	13.037	897.35	−28.18
14.012	922.31	−14.52	14.004	910.39	−19.49	14.023	898.48	−23.78
15.013	923.35	−11.89	15.013	911.48	−16.13	15.039	899.66	−20.08
16.000	924.33	−10.05	16.013	912.56	−13.58	16.011	900.77	−17.20
17.024	925.34	−8.68	17.044	913.64	−11.58	17.019	901.92	−14.80
18.001	926.31	−7.70	18.012	914.66	−10.15	18.012	903.04	−12.90
19.036	927.32	−6.90	19.015	915.70	−8.99	19.006	904.14	−11.38
20.015	928.27	−6.30	20.024	916.74	−8.07	20.035	905.27	−10.12
21.009	929.23	−5.80	21.004	917.74	−7.34	20.994	906.30	−9.15
22.027	930.22	−5.37	22.030	918.79	−6.71	22.029	907.43	−8.30
23.002	931.10	−5.02	23.027	919.77	−6.20	23.004	908.45	−7.62
24.027	932.06	−4.70	24.021	920.77	−5.77	24.034	909.57	−7.02
25.009	932.97	−4.43	25.022	921.74	−5.39	25.002	910.55	−6.53

where the corresponding standard deviations for the densities of reference fluids and periods are $\sigma_{\rho_{H2O}} = 0.003\%$,[19] $\sigma_{\rho_{N2}} = 0.02\%$,[20] $\sigma_{\tau_{H2O}} = 5 \times 10^{-6}$, $\sigma_{\tau_{N2}} = 5 \times 10^{-6}$, and $\sigma_{\tau_F} = 5 \times 10^{-6}$. The uncertainties for the densities of water and

Table 7. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
						$x_1 = 0.4068$					
	T/K = 313.16			T/K = 323.10			T/K = 333.00			T/K = 342.94	
6.028	955.07	−101.34									
7.010	956.12	−72.49	7.058	942.59	−84.48						
8.028	957.19	−46.09	8.007	943.65	−63.41	8.029	930.01	−74.16			
9.005	958.24	−19.22	9.034	944.82	−44.11	9.016	931.23	−57.14	9.055	917.41	−66.03
10.041	959.33	−10.80	10.001	945.91	−28.48	10.008	932.42	−43.01	9.984	918.63	−53.31
10.994	960.30	−8.69	11.013	947.04	−17.51	11.025	933.65	−31.18	11.061	920.01	−41.24
11.990	961.32	−7.48	12.000	948.11	−12.67	12.006	934.81	−22.63	11.996	921.23	−32.76
12.989	962.33	−6.67	12.998	949.23	−10.26	13.019	936.04	−16.90	13.050	922.57	−25.28
14.027	963.34	−6.04	13.979	950.27	−8.82	14.010	937.15	−13.50	14.076	923.82	−19.97
14.992	964.31	−5.58	15.004	951.37	−7.78	15.002	938.28	−11.34	15.011	925.00	−16.54
15.994	965.30	−5.19	16.001	952.41	−7.04	16.010	939.41	−9.84	16.021	926.20	−13.89
16.994	966.27	−4.86	16.989	953.45	−6.45	16.998	940.54	−8.76	17.029	927.42	−12.00
18.006	967.25	−4.58	18.017	954.51	−5.96	18.013	941.67	−7.91	18.001	928.58	−10.63
18.978	968.19	−4.34	18.998	955.51	−5.57	19.008	942.75	−7.24	19.026	929.79	−9.51
20.043	969.19	−4.11	20.005	956.52	−5.22	20.008	943.81	−6.69	20.073	931.01	−8.61
21.020	970.10	−3.92	20.986	957.50	−4.93	20.981	944.88	−6.24	21.008	932.09	−7.95
22.002	970.98	−3.74	22.021	958.56	−4.66	22.001	945.96	−5.84	22.005	933.21	−7.35
23.059	971.98	−3.58	22.998	959.49	−4.43	22.996	947.02	−5.50	22.992	934.31	−6.85
24.032	972.87	−3.44	23.987	960.47	−4.23	24.013	948.07	−5.19	24.049	935.49	−6.39
25.024	973.76	−3.30	25.057	961.50	−4.02	25.001	949.09	−4.93	25.062	936.61	−6.01

Table 8. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}
				$x_1 = 0.4268$				
	T/K = 313.15			T/K = 323.09			T/K = 332.98	
6.005	955.61	−107.06						
7.013	956.75	−75.92	7.005	942.62	−89.91			
8.008	957.90	−48.84	8.007	943.86	−66.44	8.015	929.54	−77.99
9.014	958.99	−19.92	9.005	944.97	−46.74	9.023	930.86	−59.74
10.006	960.05	−11.41	9.996	946.20	−29.89	9.996	932.09	−45.18
11.017	961.14	−9.04	11.020	947.43	−18.24	11.004	933.37	−32.85
12.006	962.22	−7.79	12.000	948.52	−13.23	12.004	934.65	−23.67
13.004	963.25	−6.94	13.035	949.74	−10.64	13.005	935.88	−17.71
13.997	964.28	−6.32	14.007	950.83	−9.16	14.003	937.07	−14.10
15.003	965.36	−5.82	15.007	951.95	−8.11	15.006	938.28	−11.81
16.007	966.35	−5.41	15.987	952.99	−7.34	16.024	939.46	−10.22
17.000	967.35	−5.07	16.984	954.11	−6.73	17.036	940.67	−9.08
17.994	968.36	−4.77	17.998	955.17	−6.22	18.017	941.85	−8.23
19.017	969.38	−4.51	19.040	956.31	−5.78	19.025	943.00	−7.52
19.994	970.35	−4.29	20.050	957.38	−5.42	20.004	944.10	−6.96
20.983	971.33	−4.09	21.048	958.44	−5.12	21.001	945.19	−6.48
22.024	972.32	−3.90	22.041	959.46	−4.84	21.993	946.33	−6.07
23.020	973.26	−3.73	23.037	960.49	−4.60	23.015	947.45	−5.70
24.016	974.20	−3.58	24.061	961.52	−4.38	24.114	948.62	−5.36
24.996	975.14	−3.45	25.036	962.52	−4.19	25.061	949.68	−5.10
	T/K = 342.92			T/K = 352.87			T/K = 362.75	
9.047	916.56	−69.28						
10.045	917.97	−55.03	10.008	903.63	−63.89			
11.042	919.28	−43.35	11.005	905.13	−52.23	11.002	890.57	−59.30
12.037	920.66	−33.91	12.055	906.66	−42.19	12.008	892.17	−49.54
13.020	921.93	−26.60	13.027	908.06	−34.62	13.010	893.74	−41.51
13.997	923.27	−21.22	13.995	909.43	−28.54	14.000	895.32	−34.95
14.981	924.53	−17.35	15.002	910.84	−23.57	15.027	896.84	−29.38
15.991	925.79	−14.55	16.029	912.27	−19.69	16.015	898.33	−25.05
17.002	927.11	−12.54	17.030	913.63	−16.83	17.017	899.81	−21.51
18.025	928.36	−11.03	18.010	914.96	−14.68	18.013	901.24	−18.70
19.044	929.60	−9.87	19.003	916.29	−12.98	19.024	902.72	−16.42
19.999	930.83	−9.01	20.032	917.62	−11.59	20.028	904.14	−14.60
20.984	931.96	−8.27	21.047	918.93	−10.48	21.039	905.51	−13.11
22.002	933.20	−7.64	22.005	920.15	−9.62	22.014	906.89	−11.92
23.042	934.44	−7.10	23.001	921.41	−8.87	23.027	908.24	−10.89
23.981	935.53	−6.67	24.014	922.68	−8.22			
25.047	936.75	−6.25	25.024	923.93	−7.67			

nitrogen correspond for the interval of temperature and pressure reported here. For example, for the density of DMF at 313.12 K and at 1.008 MPa, the vibration periods for water, nitrogen, and DMF are 0.819483, 0.778266, and 0.816933, respectively, whereas the densities of water and nitrogen obtained from the EoS[19,20] are 992.62 and 10.85 kg·m^{-3}, respectively. With these values and using eqs 4 to 9, a standard uncertainty of ±0.17 kg·m^{-3} is calculated for the density of DMF. Similar results are obtained for all of the densities reported in this work.

Loading of the Measurement Cell. The loading procedure for pure fluid and mixtures is based in that described in previous papers.[15,18] The samples at fixed compositions are prepared by successive loadings[18] of the pure compounds in the sapphire feeding cell with a maximum volume of 12 cm^3. The amounts of the com-

Table 9. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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/ρkg·m^{-3}	V^E/cm^3·mol^{-1}
				$x_1 = 0.4461$				
	T/K = 313.15			T/K = 323.09			T/K = 332.99	
6.022	956.18	−111.22						
6.991	957.31	−79.93	7.062	942.94	−92.38			
8.024	958.53	−50.53	7.958	944.11	−70.49			
9.006	959.66	−20.92	9.022	945.39	−48.47	9.011	930.78	−62.57
9.998	960.80	−11.91	9.998	946.60	−31.16	9.993	931.95	−47.20
10.989	961.90	−9.46	11.005	947.83	−19.14	11.013	933.65	−34.19
12.025	963.02	−8.08	12.039	949.09	−13.65	12.003	934.90	−24.71
13.003	964.12	−7.22	13.002	950.23	−11.14	13.012	936.18	−18.43
13.999	965.20	−6.56	14.007	951.42	−9.54	13.991	937.43	−14.74
14.993	966.26	−6.05	14.996	952.54	−8.45	15.009	938.71	−12.30
16.006	967.34	−5.62	16.001	953.67	−7.62	16.010	939.93	−10.67
17.007	968.38	−5.26	17.004	954.83	−6.98	17.001	941.16	−9.49
17.985	969.42	−4.96	18.000	955.98	−6.46	17.994	942.35	−8.58
19.015	970.46	−4.68	18.994	957.05	−6.03	18.988	943.52	−7.85
20.007	971.48	−4.45	20.031	958.19	−5.64	20.001	944.69	−7.24
20.996	972.47	−4.24	21.020	959.24	−5.32	20.995	945.88	−6.75
22.022	973.50	−4.05	22.029	960.34	−5.03	21.998	947.03	−6.31
22.993	974.47	−3.88	23.008	961.38	−4.79	23.023	948.19	−5.93
23.996	975.45	−3.72	24.019	962.44	−4.56	23.982	949.27	−5.62
24.992	976.41	−3.58	25.007	963.48	−4.36	25.021	950.44	−5.31

Table 10. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}	P/MPa	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
						$x_1 = 0.4502$					
	T/K = 313.16			T/K = 323.10			T/K = 333.00			T/K = 342.94	
5.026	955.28	−154.22									
5.988	956.32	−113.50									
7.004	957.42	−80.30	7.005	942.87	−94.78	7.019	928.11	−105.94	7.029	913.19	−115.71
7.999	958.57	−51.73	8.009	944.10	−69.99	8.001	929.45	−82.50	8.013	914.64	−92.34
9.031	959.69	−20.61	9.003	945.32	−49.29	9.015	930.81	−63.07	9.011	916.09	−73.61
10.012	960.79	−11.96	10.005	946.57	−31.33	10.013	932.14	−47.37	9.999	917.51	−58.61
11.036	961.92	−9.45	11.002	947.78	−19.34	11.006	933.42	−34.57	11.025	918.98	−45.86
12.022	963.01	−8.15	12.012	948.99	−13.87	12.004	934.74	−24.92	12.004	920.36	−36.01
13.014	964.13	−7.26	13.022	950.22	−11.19	13.021	936.04	−18.54	13.007	921.76	−28.10
14.015	965.19	−6.60	14.010	951.35	−9.60	14.019	937.31	−14.77	13.993	923.08	−22.35
15.005	966.24	−6.08	15.007	952.52	−8.50	15.001	938.54	−12.41	15.025	924.49	−18.09
16.019	967.32	−5.65	16.010	953.67	−7.67	16.014	939.78	−10.74	16.028	925.84	−15.20
17.003	968.34	−5.29	17.008	954.76	−7.02	17.013	941.01	−9.55	17.002	927.13	−13.17
17.999	969.40	−4.98	18.013	955.90	−6.49	18.021	942.21	−8.62	18.035	928.51	−11.57
19.033	970.43	−4.70	19.001	956.99	−6.06	19.006	943.40	−7.89	19.023	929.75	−10.38
19.978	971.41	−4.48	19.996	958.07	−5.68	20.021	944.58	−7.28	20.023	931.00	−9.43
21.007	972.47	−4.26	21.010	959.20	−5.35	21.001	945.74	−6.78	21.013	932.27	−8.65
22.023	973.48	−4.06	22.004	960.27	−5.07	22.027	946.90	−6.33	22.036	933.51	−7.99
23.040	974.49	−3.89	22.997	961.32	−4.81	23.019	948.04	−5.96	23.032	934.76	−7.44
24.007	975.45	−3.73	23.995	962.39	−4.59	24.013	949.18	−5.63	24.003	935.89	−6.97
24.995	976.42	−3.59	25.019	963.43	−4.37	25.015	950.28	−5.34	25.041	937.14	−6.54

pounds are determined with a Sartorius comparator balance (MCA1200) by mass measurements within $\pm 10^{-7}$ kg accuracy. It was periodically calibrated with a standard mass of 1 kg class E1. The estimated uncertainty for the mole fraction of the mixtures is less than $\pm 10^{-4}$.

Theory. The experimental densities of DMF were correlated using three EoS's, the 11-parameter BWRS EoS,[12]

$$P = \frac{RT}{V} + \frac{(B_0RT - A_0 - C_0/T^2 + D_0/T^3 - E_0/T^4)}{V^2} + \frac{(bRT - a - d/T)}{V^3} + \frac{\alpha(a + d/T)}{V^6} + \frac{c(1 + u/V^2)\exp(-u/V^2)}{V^3T^2} \tag{10}$$

where V is the molar volume and the units for the corresponding constants are shown in Table 2, and the Tait equation,[13] which is expressed as follows

$$\rho = \frac{\rho_0}{1 - C\ln\dfrac{(B_T + P)}{(B_T + P_0)}} \tag{11}$$

where ρ_0 is given as a modified Rackett equation[13]

$$\rho_0 = \frac{A_R}{B_R^{[1+(1-T/C_R)^{D_R}]}} \tag{12}$$

P_0 is a reference pressure equal to 0.1 MPa, and B_T in the Tait equation is expressed as[13]

$$B_T = b_0 + b_1\frac{T}{E} \tag{13}$$

where E is a constant taken to be equal to 100 as reported by Ihmels and Gmehling.[13] Densities for DMF at atmospheric pressure reported in the literature[8,9,22–26] were correlated to obtain constants A_R, B_R, C_R, and D_R of eq 12.

Because excellent results were obtained for liquid densities of decane and CO_2 + decane mixtures in a previous paper,[14] a five-parameter empirical equation was used to correlate the densities of DMF and CO_2 + DMF mixtures. This equation is a modification of eq 12 from the paper by Toscani and Szwarc[27] and is expressed as follows

$$V = \frac{c_1 + c_2 P}{c_3 - (c_4/T + c_5/T^{1/3}) + P} \tag{14}$$

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 DMF reported in this work.

The different statistical values used to evaluate the correlations are defined by the following equations:

$$\%\Delta V = 100\left(\frac{V_{\mathrm{exptl}} - V_{\mathrm{calcd}}}{V_{\mathrm{exptl}}}\right) \tag{15}$$

$$\mathrm{ADD} = \frac{1}{n}\sum_{i=1}^{n}|\%\Delta V_i| \tag{16}$$

$$\mathrm{bias} = \frac{1}{n}\sum_{i=1}^{n}(\%\Delta V_i) \tag{17}$$

$$\mathrm{SDV} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\%\Delta V_i - \mathrm{bias})^2} \tag{18}$$

$$\mathrm{RMS} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\%\Delta V_i)^2} \tag{19}$$

The values for the different correlations are reported in Tables 2, 3, 14, and 15.

Results and Discussion

Compressed liquid densities of DMF at six different temperatures from (313 to 363) K and pressures up to 25 MPa are reported in Table 1. The BWRS EoS,[12] the Tait equation,[13] and eq 14 were used to correlate the experimental densities using the same procedure detailed in a previous paper.[15] The parameters fitted to experimental densities of DMF reported in this work for the three equations and their statistical values are given in Tables 2, 3, and 14. Relative deviations $100(V^{\mathrm{exptl}} - V^{\mathrm{calcd}})/V^{\mathrm{exptl}}$ for DMF using eq 14 and the BWRS EoS are plotted in Figure 2. Equation 14 gave similar deviations to those obtained with the multiparametric BWRS EoS. For the Tait equation, the maximum relative deviations are +0.26% and −0.12%. The deviations are larger for this equation because the correlation for the racket term was done for the interval (298.15 to 318.15) K and this introduces deviations into the extrapolation at higher temperatures in the calculation of the experimental densities.

Equation 14 is extrapolated to lower temperatures to calculate the densities of DMF reported by Scherlin et al.[8] The values calculated by eq 14 were compared to experimental data reported by Scherlin et al.,[8] and a maximum relative deviation of $-0.18\ \mathrm{kg \cdot m^{-3}}$ was found in density at temperatures from (283.15 to 318.15) K. These results are shown in Table 4. Densities of DMF from (323.15 to 373.15) K at atmospheric pressure calculated with eq 14 are also reported in Table 4. Because of the absence of data for making comparisons under these conditions, and consider-

Table 11. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}
				$x_1 = 0.6235$				
	T/K = 313.13			T/K = 323.07			T/K = 332.96	
8.014	949.79	−69.68						
9.041	952.04	−26.92	9.001	928.72	−66.58			
10.057	954.25	−15.14	10.031	931.44	−41.17	10.005	907.82	−63.63
10.998	956.28	−12.04	11.013	933.93	−25.09	10.991	910.93	−46.10
11.991	958.34	−10.24	12.042	936.47	−17.58	12.056	913.98	−32.02
12.985	960.34	−9.05	13.033	938.86	−14.07	13.000	916.59	−23.99
14.000	962.36	−8.15	13.992	941.10	−12.00	14.042	919.37	−18.63
14.996	964.28	−7.47	14.972	943.31	−10.54	15.010	921.91	−15.51
16.016	966.23	−6.90	15.993	945.57	−9.42	15.997	924.40	−13.33
16.993	968.02	−6.45	16.998	947.71	−8.56	17.030	926.91	−11.69
18.006	969.86	−6.05	18.015	949.84	−7.87	18.038	929.31	−10.47
18.988	971.70	−5.72	18.988	951.84	−7.32	19.028	931.63	−9.53
20.033	973.47	−5.40	20.012	953.89	−6.83	20.027	933.85	−8.75
21.061	975.25	−5.13	21.005	955.83	−6.42	21.009	936.05	−8.11
22.021	976.88	−4.90	22.029	957.78	−6.05	22.009	938.17	−7.56
22.996	978.52	−4.70	23.012	959.63	−5.74	23.042	940.35	−7.07
24.001	980.14	−4.50	24.020	961.47	−5.45	24.041	942.44	−6.66
25.034	981.79	−4.32	24.979	963.24	−5.21	25.008	944.38	−6.31
	T/K = 342.89			T/K = 352.81			T/K = 362.68	
10.992	886.15	−61.42						
12.012	889.74	−47.30	11.994	863.79	−59.08			
13.020	893.05	−36.44	13.017	868.11	−47.55			
14.010	896.16	−28.59	14.003	871.85	−38.65	13.997	842.98	−47.09
15.018	899.25	−22.96	15.051	875.54	−31.29	15.019	847.62	−39.21
16.005	902.14	−19.10	16.021	878.85	−26.10	16.021	851.83	−32.98
17.023	905.02	−16.26	17.011	882.12	−22.07	16.992	855.82	−28.15
18.015	907.74	−14.21	18.025	885.31	−18.94	18.022	859.78	−24.07
19.032	910.42	−12.60	19.034	888.42	−16.54	19.000	863.40	−21.00
20.044	913.05	−11.34	20.027	891.37	−14.69	20.047	867.10	−18.37
21.008	915.46	−10.36	20.969	894.02	−13.26	21.057	870.49	−16.33
21.997	917.87	−9.53	22.044	897.02	−11.95	22.005	873.58	−14.76
23.022	920.31	−8.81	22.987	899.54	−10.99	22.981	876.69	−13.42
24.005	922.57	−8.21	24.010	902.21	−10.11	24.005	879.78	−12.23
25.050	924.92	−7.67	25.062	904.90	−9.34	24.998	882.71	−11.26

Table 12. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}
				$x_1 = 0.8091$				
	T/K = 313.14			T/K = 323.08			T/K = 332.97	
9.015	920.03	−33.74						
9.992	923.92	−17.94						
11.003	927.79	−13.55	11.047	888.99	−29.27			
12.022	931.54	−11.24	12.004	893.47	−20.32			
13.011	934.99	−9.77	13.042	898.20	−15.60	13.046	858.28	−27.18
14.003	938.37	−8.69	14.006	902.33	−12.99	14.016	863.75	−20.90
15.006	941.63	−7.85	15.005	906.31	−11.15	15.002	869.06	−16.88
16.000	944.75	−7.18	16.016	910.13	−9.79	16.027	874.28	−14.10
16.988	947.80	−6.63	16.989	913.66	−8.78	17.017	879.06	−12.18
18.019	950.82	−6.14	18.023	917.28	−7.92	18.042	883.74	−10.68
18.996	953.63	−5.74	18.997	920.57	−7.26	19.003	887.97	−9.59
20.032	956.51	−5.37	20.018	923.89	−6.67	20.021	892.23	−8.65
21.035	959.25	−5.06	21.002	927.01	−6.19	21.029	896.31	−7.89
21.995	961.81	−4.80	22.041	930.23	−5.75	22.019	900.16	−7.26
23.033	964.52	−4.54	22.980	933.13	−5.41	23.004	903.83	−6.73
24.015	966.98	−4.32	23.989	936.00	−5.08	24.041	907.60	−6.25
25.006	969.42	−4.12	25.049	939.12	−4.77	24.998	910.97	−5.86
	T/K = 342.92			T/K = 352.86			T/K = 362.79	
15.061	832.64	−25.50						
15.988	839.54	−21.08	16.031	799.40	−28.94			
17.027	845.55	−17.48	17.002	806.61	−24.09			
18.016	851.10	−14.99	18.047	814.20	−20.18	18.033	777.33	−26.19
19.028	856.53	−13.06	19.050	820.88	−17.34	19.005	784.90	−22.51
20.057	861.77	−11.54	20.005	827.13	−15.24	20.003	792.49	−19.53
21.012	866.52	−10.42	21.045	833.27	−13.40	21.014	799.75	−17.11
21.992	871.08	−9.46	22.052	839.08	−11.99	22.017	806.50	−15.18
22.999	875.54	−8.64	23.029	844.25	−10.86	23.043	813.10	−13.56
24.029	879.90	−7.93	24.015	849.31	−9.90	24.052	819.28	−12.25
25.020	883.99	−7.35	25.051	854.32	−9.05	25.083	825.05	−11.12

Table 13. Experimental Densities and Excess Molar Volumes for the CO_2 (1) + DMF (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}
				$x_1 = 0.9311$				
	T/K = 313.14			T/K = 323.09			T/K = 332.98	
10.006	835.47	−15.44						
11.013	846.13	−10.89						
12.041	855.75	−8.60	12.017	797.65	−17.58			
13.017	864.01	−7.23	13.010	810.33	−12.94	13.019	744.38	−24.22
14.036	871.87	−6.23	14.016	821.48	−10.27	14.011	761.83	−17.75
15.031	878.95	−5.50	15.005	831.25	−8.56	15.009	776.41	−13.81
16.006	885.43	−4.93	16.036	840.41	−7.31	16.030	789.22	−11.20
17.030	891.82	−4.46	17.025	848.46	−6.42	17.017	800.11	−9.45
17.988	897.48	−4.09	18.021	855.96	−5.72	18.002	809.93	−8.16
19.037	903.28	−3.75	19.034	863.06	−5.14	19.031	819.29	−7.14
20.022	908.47	−3.47	20.010	869.50	−4.69	20.025	827.57	−6.36
21.000	913.41	−3.24	21.029	875.82	−4.29	21.030	835.37	−5.72
22.002	918.23	−3.03	22.009	881.60	−3.97	21.994	842.35	−5.22
23.016	922.92	−2.84	23.050	887.36	−3.67	22.998	849.15	−4.77
24.006	927.35	−2.68	23.995	892.39	−3.44	24.024	855.75	−4.39
25.020	931.70	−2.53	25.056	897.78	−3.20	25.011	861.78	−4.07
	T/K = 342.92			T/K = 352.86			T/K = 362.73	
15.034	711.76	−21.30						
16.002	729.81	−16.99						
17.015	745.62	−13.83	17.024	684.50	−18.89			
18.024	759.30	−11.58	18.005	702.67	−15.79	18.005	641.86	−19.62
19.002	770.95	−9.95	19.028	718.94	−13.33	19.024	662.81	−16.72
20.000	781.74	−8.68	20.001	732.41	−11.51	20.021	680.44	−14.42
21.034	791.87	−7.64	21.006	744.94	−10.04	21.028	696.02	−12.55
22.002	800.53	−6.85	22.024	756.39	−8.85	22.008	709.54	−11.06
23.014	809.02	−6.18	23.012	766.47	−7.91	23.017	722.12	−9.81
24.017	816.82	−5.62	23.999	775.83	−7.14	24.029	733.65	−8.77
25.008	824.06	−5.16	25.019	784.81	−6.47	25.019	744.01	−7.92

ing the relative deviations obtained at lower temperatures between experimental and calculated densities, similar behavior can be expected at temperatures higher than 318.15 K; however, this statement must be probed in the future.

Compressed liquid densities and excess molar volumes for the CO_2 + DMF mixtures from (313 to 363) K and pressures up to 25 MPa are presented in Tables 5 to 13 for nine different compositions.

The parameters obtained by correlating the densities of DMF and CO_2 + DMF mixtures using eq 14 are reported in Tables 14 and 15. The error in the correlation of the densities increases as the composition of CO_2 in the mixture is increased. This behavior is similar to previous results.[14]

Table 14. Parameters for Equation 14 for Data Reported in This Work

	DMF	$x_1 = 0.2618$	$x_1 = 0.2876$	$x_1 = 0.4068$	$x_1 = 0.4268$
$T_{\min}$/K	313.12	313.16	313.15	313.16	313.15
$T_{\max}$/K	362.67	333.00	362.75	342.94	362.75
$P_{\min}$/MPa	1.008	3.057	4.032	6.028	6.005
$P_{\max}$/MPa	25.056	25.038	25.023	25.062	25.061
$\rho_{\min}$/kg·m^{-3}	882.04	923.54	891.20	917.41	890.57
$\rho_{\max}$/kg·m^{-3}	945.35	964.27	966.15	973.76	975.14
data points	150	68	119	74	103
c_1/MPa·kg^{-1}·m^3	0.221338	0.175480	0.154355	0.133045	0.119142
c_2/kg^{-1}·m^3	9.124×10^{-4}	8.863×10^{-4}	8.979×10^{-4}	8.874×10^{-4}	8.951×10^{-4}
c_3/MPa	−346.628	−362.533	−392.245	−391.225	−374.858
c_4/K·MPa	55 160.410	51 477.690	56 064.700	53 106.570	50 200.510
c_5/MPa·K$^{1/3}$	−4947.3870	−4702.5200	−4869.4760	−4664.9520	−4401.3990
AAD/%	0.0060	0.0017	0.0031	0.0025	0.0072
bias/%	-1.01×10^{-6}	-5.90×10^{-7}	-4.75×10^{-7}	-6.57×10^{-7}	-1.65×10^{-6}
SDV/%	8.42×10^{-5}	6.16×10^{-6}	3.56×10^{-5}	1.86×10^{-5}	1.28×10^{-4}
RMS/%	0.0072	0.0020	0.0040	0.0032	0.0089

Table 15. Parameters for Equation 14 for Data Reported in This Work

	$x_1 = 0.4461$	$x_1 = 0.4502$	$x_1 = 0.6235$	$x_1 = 0.8091$	$x_1 = 0.9311$
$T_{\min}$/K	313.15	313.16	313.13	313.14	313.14
$T_{\max}$/K	332.99	342.94	362.68	362.79	362.73
$P_{\min}$/MPa	6.022	5.026	8.014	9.016	10.006
$P_{\max}$/MPa	25.021	25.041	25.062	25.083	25.056
$\rho_{\min}$/kg·m^{-3}	930.78	913.19	842.98	777.73	641.86
$\rho_{\max}$/kg·m^{-3}	976.41	976.42	981.79	969.42	931.70
data points	56	78	92	74	71
c_1/MPa·kg^{-1}·m^3	0.122905	0.120817	0.039001	0.015331	0.000841
c_2/kg^{-1}·m^3	8.842×10^{-4}	8.874×10^{-4}	9.318×10^{-4}	9.601×10^{-4}	1.003×10^{-3}
c_3/MPa	−414.835	−381.527	−496.566	−344.162	−481.550
c_4/K·MPa	55 812.220	50 435.770	68 193.660	40 359.730	64 015.330
c_5/MPa·K$^{1/3}$	−4819.0100	−4462.8840	−5095.9140	−3300.7560	−4651.6070
AAD/%	0.0036	0.0048	0.0504	0.1004	0.1853
bias/%	-5.83×10^{-7}	-8.50×10^{-7}	-8.51×10^{-5}	-2.66×10^{-4}	-1.21×10^{-3}
SDV/%	1.01×10^{-4}	1.18×10^{-4}	8.73×10^{-3}	1.97×10^{-2}	1.17×10^{-1}
RMS/%	0.0053	0.0065	0.0652	0.1151	0.2465

Because experimental measurement densities of DMF and its mixtures with CO_2 were obtained, the excess volumes were calculated according to the relation

$$V^{E} = \frac{x_1 W_1 + x_2 W_2}{\rho^{\mathrm{mix}}} - (x_1 V_1 + x_2 V_2) \tag{20}$$

where V^E is the excess molar 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 weighs of CO_2 and DMF, respectively, and x_1 and x_2 are the mole fractions of CO_2 and DMF, respectively. V_1 is calculated using the Span and Wagner EoS,[28] and V_2 is calculated using the BWRS EoS[12] with the parameters given in Table 2. As shown in Figure 3, excess molar volumes become less negative as pressure increases at constant temperature. Besides, these volumes become more negative as temperature increases at constant pressure, as can be observed in Figure 4. In both cases, the minimum values of the excess volumes are found at higher CO_2 concentrations, and these behaviors apply to all isobaric and isothermal data reported here.

Conclusions

New compressed liquid densities of DMF and CO_2 + DMF binary mixtures at temperatures from (313 to 363) K and pressures up to 25 MPa at nine different compositions are reported. The BWRS EoS was used to correlate the experimental densities of DMF, giving a standard deviation equal to 0.0097%, whereas the Tait equation gave a standard deviation equal to 0.0209%. It was found that the Tait equation requires densities at atmospheric pressure at the same interval of temperature of the high-pressure densities in order to obtain the parameters of the Rackett term. A simple five-parameter equation was tested successfully to represent the densities of the systems reported in this work; this equation has the advantage of representing the compressed liquid region with half the number of parameters as the BWRS EoS with the same accuracy. Because eq 14 is explicit in volume, its implementation for industrial applications does not require great programming effort and computer time. This equation is also capable of extrapolating densities at atmospheric conditions and does not required data at some reference condition as the Tait equation does. The propagation of uncertainties was presented for the determination of densities using a VTD with the classical method of calibration. The calculated excess molar volumes have a negative trend for all of these systems under the reported experimental conditions.

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