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Densities of Carbon Dioxide + Methanol Mixtures at Temperatures from 313.2 to 323.2 K and at Pressures from 10 to 20 MPa

Richard L. Smith, Jr.,* Sung B. Lee, Sachio Suzuki, Chie Saito, Hiroshi Inomata, and Kunio Arai

Research Center of Supercritical Fluid Technology, Department of Chemical Engineering, Tohoku University,
Aoba-ku, Aza Aramaki Aoba-07, Sendai 980-8579 Japan

Densities of carbon dioxide (1) + methanol (2) mixtures were measured with a variable-volume static type of apparatus at three temperatures (313.2, 318.2, and 323.2 K) over a range of pressures (10 to 20 MPa) for methanol-rich mole fractions ($x_2 > 0.257$). Molar volumes could be correlated to within about ±0.1 cm^3·mol^{-1} by combining a Redlich−Kister expression with a Tait type of equation.

Introduction

The addition of compressed gases to polar liquids leads to an enhancement in the fluid properties such as viscosity, diffusion coefficient, and density and this effect is being studied for new chromatographic applications[1] and for particle design with gas antisolvent techniques.[2] Methanol and carbon dioxide are two of the most widely used solvent pairs and, thus, properties of these mixtures are of great interest. Some of the studies that have been made on methanol−CO_2 systems include Frank et al.[3] who measured diffusion coefficients and viscosities, Dai et al.,[4] who measured excess enthalpies, and Yeo et al.,[5] who measured critical properties. Bezanehtak et al.[6] summarize vapor−liquid equilibria of methanol−CO_2 systems. Densities at various compositions and temperatures of methanol in the presence of carbon dioxide have been measured by Roškar et al.,[7] Chang et al.,[8] Galicia-Luna et al.,[9,10] and Goldfarb et al.[11] We have begun to measure dielectric spectra of methanol−CO_2 mixtures,[12] and in the data reduction, the mixture density is needed. As a result, we have measured densities of methanol−CO_2 mixtures at temperatures from 313.2 K to 323.2 K at pressures from 10 MPa to 20 MPa with emphasis on compositions in the methanol-rich region. In this work, our objective is to report on our methanol−CO_2 density measurements and to provide a suitable correlating equation for the data.

Experimental Section

Materials. Anhydrous methanol (99.8%) and water (HPLC-grade) were obtained from Wako Pure Chemicals (Osaka) and were handled to avoid contamination with air and moisture. Methanol purity was checked with gas chromatography. CO_2 (99.99%) was obtained Nihon Sanso (Sendai) and was dried by passing the gas through a column of silica gel and then filtered with a 0.5-μm sintered filter.

Apparatus. The apparatus used for the density measurements was developed in our research on dielectric spectra and uses a vibrating tube densimeter (model DMA 512 P and DMA 60, Anton Paar, Graz).[12,13] The vibration period of the tube and its contents are proportional to the square root of its mass times an instrument constant that is determined by measurement of the vibration period for known reference fluids at given conditions of temperature and pressure. The calibration procedure is described in the next section. The apparatus consisted of a variable volume (≈110 cm^3) static system in which a magnetic pump was used to circulate CO_2 and methanol mixtures through the densimeter until equilibrium was reached. The entire apparatus was enclosed in a constant temperature forced convection air bath (model FV-450, Advantec, Tokyo) in which temperature was controlled to within ±0.1 K. Further details are given in ref 13.

Temperature was measured inside the system and outside of the system with a three-wire platinum resistance thermometer (PRT) (model TF-A31, Keyence, Osaka) and a four-wire PRT (model RMB-100SY02, Yamari, Osaka), respectively. Accuracy of the temperature probes was confirmed within the system by comparison with a secondary temperature standard that was NIST traceable to 0.01 K. Temperature gradients in the system were no greater than 0.05 K. Pressure of the system was measured with a digital sensor (model SPX-G, Sokken, Tokyo) to an accuracy of 0.05 MPa. Accuracy of the pressure sensor was confirmed by comparison with a dead weight tester that was accurate to 0.5 kPa. Temperatures and pressures reported are estimated to have reproducibilities of ±0.12 K and ±0.07 MPa, respectively, due to gradual temperature and pressure cycling of the system. Composition of the system was determined by trapping the entire system contents in a 125-cm^3 bomb with liquid nitrogen that was followed by weighing the loaded substances before and after slow depressurization into a second trap filled with water. Compositions reported are estimated to be accurate to 0.005 in mole fraction. Replicate measurements and some analyses are given in the discussion.

Calibration. In this work, air, water, and methanol were used as the reference fluids. Air was used as a reference fluid at atmospheric pressure with properties being determined from the Kyushu University physical property package PROPATH.[14] Pure water and pure methanol were used as reference fluids at pressures up to 20 MPa with properties being determined from the IAPWS-95 formulation of Pruβ and Wagner[15] and the IUPAC equation of state of de Reuck and Craven,[16] respectively. It was noticed that some curvature existed between pure water, pure methanol, and air at atmospheric pressures.

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* To whom correspondence should be addressed. E-mail: smith@scf.che.tohoku.ac.jp. Fax: +81-22-217-7293.

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Table 1. Experimental Densities for the CO_2 (1) + Methanol (2) System at 313.2 K

P MPa	x_2	ρ $kg \cdot m^{-3}$	V_{mix} $cm^3 \cdot mol^{-1}$	V_{mix} (eq 4) $cm^3 \cdot mol^{-1}$	deviation (eq 4) %
10.50	0.580	845.39	43.848	43.876	0.064
10.56	0.580	845.34	43.851	43.867	0.037
10.57	0.580	845.41	43.847	43.866	0.043
10.89	0.580	846.19	43.806	43.819	0.028
10.95	0.630	843.03	43.261	43.244	−0.039
10.96	0.630	842.87	43.269	43.242	−0.062
10.96	0.630	842.96	43.264	43.242	−0.051
10.97	0.630	843.00	43.262	43.241	−0.049
11.01	0.580	846.43	43.794	43.801	0.017
11.02	0.580	846.59	43.786	43.800	0.032
11.03	0.580	846.56	43.787	43.799	0.025
11.08	0.720	835.34	42.370	42.364	−0.014
11.09	0.720	835.45	42.364	42.363	−0.004
11.12	0.720	835.57	42.358	42.360	0.005
11.14	0.810	823.90	41.651	41.687	0.087
11.16	0.810	824.05	41.643	41.686	0.102
11.18	0.720	835.74	42.350	42.355	0.013
11.18	0.810	824.13	41.639	41.684	0.108
11.18	0.810	824.16	41.638	41.684	0.112
12.41	0.630	846.32	43.093	43.076	−0.039
12.41	0.630	846.28	43.095	43.076	−0.043
12.42	0.630	846.34	43.091	43.075	−0.038
12.43	0.630	846.37	43.090	43.074	−0.038
12.90	0.810	826.27	41.531	41.567	0.086
12.97	0.580	851.86	43.515	43.531	0.037
12.97	0.810	826.43	41.523	41.562	0.094
12.99	0.810	826.51	41.519	41.561	0.100
13.00	0.810	826.55	41.517	41.560	0.104
13.01	0.580	851.92	43.512	43.526	0.032
13.02	0.580	851.93	43.511	43.524	0.030
13.03	0.580	852.00	43.508	43.523	0.035
13.11	0.630	847.80	43.017	42.999	−0.043
13.11	0.630	847.80	43.017	42.999	−0.043
13.18	0.630	848.11	43.002	42.991	−0.024
13.18	0.720	838.68	42.201	42.185	−0.038
13.26	0.630	848.28	42.993	42.983	−0.025
13.27	0.720	838.95	42.187	42.177	−0.024
13.29	0.720	839.03	42.183	42.176	−0.018
13.29	0.720	838.99	42.186	42.176	−0.023
14.83	0.580	856.43	43.283	43.295	0.028
14.88	0.580	856.53	43.278	43.289	0.025
14.88	0.810	828.55	41.417	41.437	0.048
14.89	0.720	841.22	42.073	42.047	−0.063
14.89	0.810	828.57	41.416	41.436	0.049
14.89	0.810	828.58	41.415	41.436	0.051
14.90	0.720	841.22	42.074	42.046	−0.066
14.92	0.720	841.24	42.073	42.044	−0.067
15.02	0.580	856.89	43.259	43.272	0.028
15.11	0.580	857.32	43.238	43.261	0.053
15.11	0.720	841.87	42.041	42.029	−0.028
15.26	0.630	852.20	42.795	42.773	−0.051
15.30	0.630	852.28	42.791	42.769	−0.052
15.32	0.630	852.31	42.790	42.767	−0.052
15.34	0.630	852.35	42.788	42.765	−0.052
15.35	0.630	852.46	42.782	42.764	−0.042
16.81	0.810	830.58	41.316	41.316	0.000
16.87	0.810	830.72	41.309	41.312	0.008
16.92	0.580	861.55	43.026	43.049	0.055
16.92	0.810	830.81	41.304	41.309	0.013
16.94	0.580	861.61	43.022	43.047	0.058
16.95	0.580	861.68	43.019	43.046	0.062
16.99	0.580	861.74	43.016	43.041	0.060
17.05	0.720	844.50	41.910	41.881	−0.070
17.07	0.720	844.53	41.908	41.879	−0.069
17.09	0.720	844.58	41.906	41.878	−0.067
17.10	0.720	844.64	41.903	41.877	−0.062
17.13	0.720	844.74	41.898	41.875	−0.055
17.69	0.630	857.15	42.548	42.537	−0.026
18.03	0.630	857.72	42.520	42.506	−0.033
18.06	0.630	857.78	42.517	42.503	−0.033
18.09	0.630	857.87	42.512	42.500	−0.028

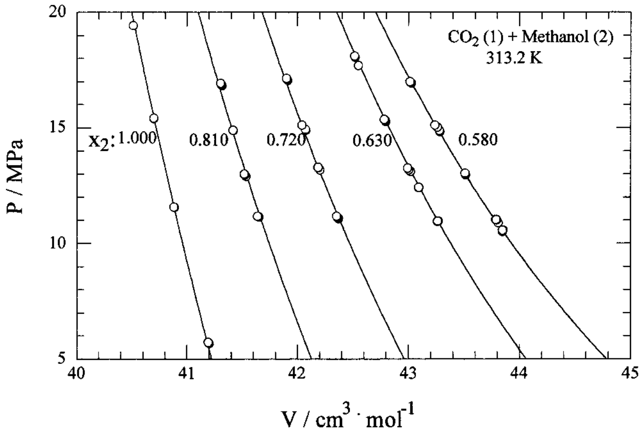

Figure 1. Pressure−volume diagram for the CO_2 (1) + methanol (2) system at 313.2 K; lines calculated from eq 4.

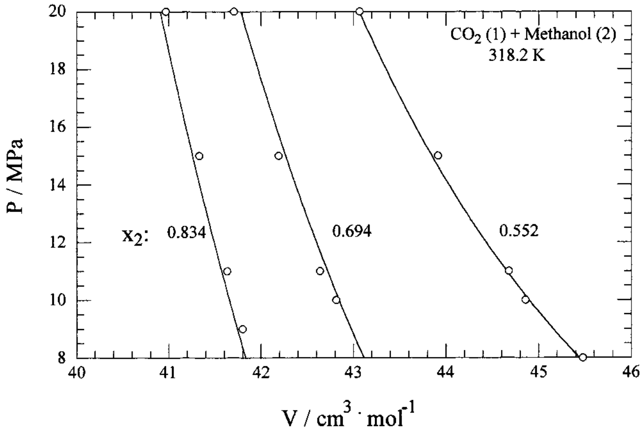

Figure 2. Pressure−volume diagram for the CO_2 (1) + methanol (2) system at 318.2 K; lines calculated from eq 4.

Since all measurements were at super-atmospheric conditions and at methanol-rich mole fractions, methanol and water were used mainly in regressing the constants for the calibration equations at a given temperature. The form of the calibration equations were

$$\rho = AT^2 + BT + C + DT^2P \qquad (1)$$

where ρ ($kg \cdot m^{-3}$) is the density, T is the period (s), P is the absolute pressure (MPa), and A, B, C, and D are fitted parameters in consistent units. At each temperature, 60 to 70 points were used to determine the constants in eq 1, and in all fits, maximum deviations were less than 0.05% with many deviations being less than 0.01%. For all temperatures, the 95% confidence interval of the density residuals contained zero.

Results and Discussion

Tables 1−3 show the experimental data at 313.2 K, 318.2 K, and 323.2 K, respectively. The correlated values and the residuals are discussed in the next section. From the data, it can be seen that all densities in the range of 750 to 870 $kg \cdot m^{-3}$, which is intermediate to those of pure methanol and pure water at the same temperature and pressure. The methanol and CO_2 system exhibits a maximum in density versus composition for a given temperature and pressure[17] and thus pressure−molar volume plots show the trend of the data more clearly. A maximum in density for the 2-propanol and CO_2 system has also been noted by Yaginuma et al.[18] Figures 1−3 show all data plotted in $P-V$ coordinates at given mole fractions of methanol. From the

Table 2. Experimental Densities for the CO_2 (1) + Methanol (2) System at 318.2 K

P	x_2	ρ	V_{mix}	V_{mix} (eq 4)	deviation (eq 4)
MPa		kg·m^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	%
8.0	0.552	822.37	45.477	45.440	−0.080
9.0	0.834	814.10	41.799	41.744	−0.132
10.0	0.552	833.71	44.859	44.897	0.085
10.0	0.694	833.84	42.813	42.846	0.077
11.0	0.552	837.04	44.680	44.657	−0.052
11.0	0.694	837.25	42.639	42.721	0.192
11.0	0.834	817.35	41.633	41.573	−0.144
15.0	0.552	851.62	43.915	43.847	−0.154
15.0	0.694	846.17	42.190	42.266	0.182
15.0	0.834	823.35	41.330	41.259	−0.172
20.0	0.552	868.44	43.064	43.063	−0.003
20.0	0.694	855.99	41.705	41.781	0.182
20.0	0.834	830.59	40.969	40.908	−0.150

Table 3. Experimental Densities for the CO_2 (1) + Methanol (2) System at 323.2 K

P	x_2	ρ	V_{mix}	V_{mix} (eq 4)	deviation (eq 4)
MPa		kg·m^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	%
11.00	0.257	748.05	54.721	54.579	−0.260
11.51	0.257	759.51	53.896	53.894	−0.002
12.61	0.257	776.47	52.718	52.738	0.037
13.20	0.257	784.57	52.174	52.236	0.120
14.17	0.257	794.05	51.551	51.533	−0.035
14.74	0.257	800.56	51.132	51.173	0.081
15.51	0.257	806.00	50.787	50.736	−0.101
15.96	0.257	810.05	50.533	50.501	−0.063
16.57	0.257	814.88	50.233	50.205	−0.057
17.16	0.257	819.23	49.966	49.938	−0.056
17.78	0.257	823.58	49.703	49.677	−0.052
18.25	0.257	826.84	49.507	49.490	−0.034
11.20	0.288	769.29	52.728	52.695	−0.063
11.90	0.288	777.90	52.145	52.139	−0.012
12.10	0.331	795.59	50.338	50.324	−0.029
12.65	0.331	800.73	50.015	50.065	0.101
13.40	0.331	806.56	49.653	49.741	0.176
14.65	0.331	814.48	49.171	49.258	0.178
15.78	0.331	821.89	48.727	48.872	0.297
16.95	0.331	829.12	48.303	48.512	0.433
15.31	0.380	824.71	47.850	47.741	−0.226
18.14	0.380	839.56	47.003	47.060	0.122
10.57	0.486	817.09	46.743	46.654	−0.191
11.00	0.486	819.64	46.598	46.551	−0.101
11.15	0.486	819.63	46.598	46.515	−0.178
12.07	0.486	823.23	46.395	46.307	−0.188
12.09	0.486	825.25	46.281	46.303	0.046
13.12	0.486	827.25	46.169	46.085	−0.183
11.00	0.570	823.34	45.168	45.237	0.153
13.00	0.570	828.19	44.903	44.902	−0.003
15.00	0.570	833.26	44.630	44.598	−0.071
17.00	0.570	837.79	44.389	44.322	−0.151
20.00	0.570	844.14	44.055	43.947	−0.244
13.00	0.700	821.39	43.381	43.499	0.271
15.00	0.700	825.14	43.184	43.274	0.209
17.00	0.700	829.15	42.974	43.064	0.209
20.00	0.700	834.91	42.678	42.775	0.226
10.50	0.880	796.86	42.013	42.086	0.174
11.00	0.880	796.83	42.014	42.041	0.064
13.00	0.880	800.29	41.833	41.868	0.086
15.00	0.880	802.69	41.708	41.705	−0.006
17.00	0.880	805.35	41.570	41.550	−0.047
20.00	0.880	808.84	41.391	41.333	−0.140
10.70	0.940	785.76	41.693	41.674	−0.045
11.00	0.940	786.19	41.670	41.649	−0.049
13.00	0.940	788.61	41.542	41.492	−0.121
15.00	0.940	790.77	41.428	41.342	−0.209
17.00	0.940	793.16	41.304	41.200	−0.252
20.00	0.940	796.43	41.134	40.998	−0.329

figures, it can be seen that the methanol liquid $P-V$ lines had very steep slopes for methanol mole fractions of about 0.5 or higher. However, as the CO_2 mole fraction increased, the $P-V$ lines exhibited greater curvature.

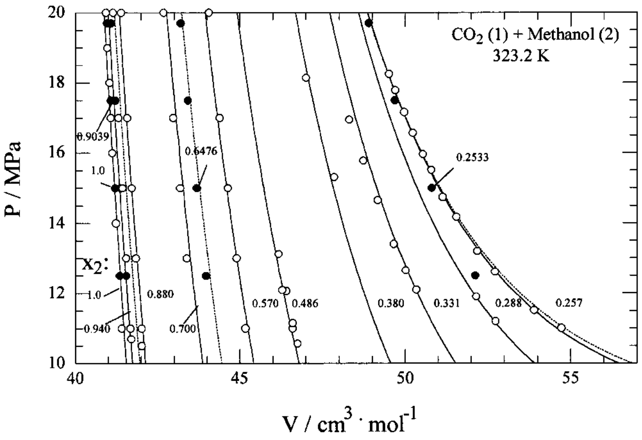

Figure 3. Pressure−volume diagram for the CO_2 (1) + methanol (2) system at 323.2 K; white circles, this work; filled circles, Galicia-Luna et al.;[9,10] lines calculated from eq 4; dashed lines calculated from eq 4 at compositions of ref 9.

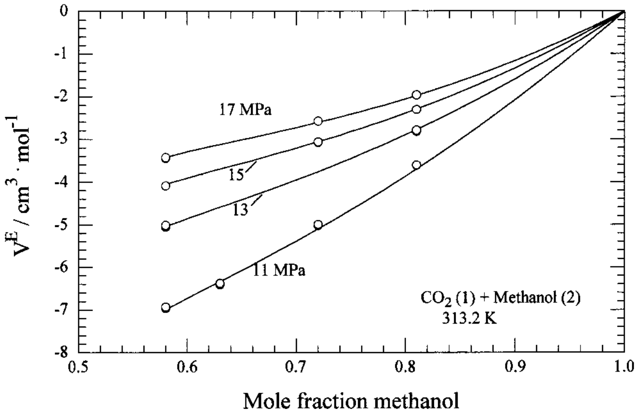

Figure 4. Excess molar volumes for the CO_2 (1) + methanol (2) system at 313.2 K; lines calculated from eq 4.

The precision of the data can be estimated from replicate measurements made at 313.2 K. From Table 1 and Figure 1, maximum variabilities of 0.1 kg·m^{-3} were observed by comparing density measurements made at the same pressures or pressures within about 0.01 MPa. In general, the variations in the density were much less than 0.1 kg·m^{-3}. Due to errors in the mole fraction determination and temperature and pressure cycling in the system, however, accuracy in density is estimated to be no higher than about 0.5 kg·m^{-3} with the higher errors occurring for the higher CO_2 mole fractions.

Some measurements were performed at specific pressures of nominally 11, 13, 15, 17, and 20 MPa to allow analysis of the excess molar volumes. Pure component molar volumes were obtained from the equations of Span and Wagner[19] for pure CO_2 and IUPAC relations of de Reuck and Craven[16] for pure methanol. Results are shown plotted in Figures 4−6 along with correlation equation results. The excess volumes can be seen to be negative over the composition region measured. Development of the correlation equations is discussed next.

Correlation. Data correlation was somewhat more difficult than at first anticipated. Forms of the Tait equation can be fitted to the experimental data at a given composition but do not allow interpolation at other compositions. The excess volumes at a given temperature and pressure can be fit with Redlich−Kister expansions or remarkably well with van-Laar-type expressions but do not allow interpolation at other pressures. Since our objective

Table 4. Parameter Values for Eq 4 and Their Standard Deviation

	313.2 K		318.2 K		323.2 K	
parameter	values	standard deviation	values	standard deviation	values	standard deviation
P_0 (MPa)	11		11		11	
c	0.07		0.07		0.07	
A_1 (cm^3·mol^{-1})	−11.92293	0.095	−19.22192	0.585	−63.90117	1.249
A_2 (cm^3·mol^{-1})	0		0		−48.13704	1.527
A_3 (cm^3·mol^{-1})	0		0		−25.21391	1.189
V_1 (cm^3·mol^{-1})	54.71537	0.062	59.56155	0.349	83.07311	0.612
V_2 (cm^3·mol^{-1})	40.90840	0.002	41.18354	0.025	41.46474	0.012
B_1 (MPa)	−41.32487	0.939	−39.67061	4.277	−21.30546	0.378
B_2 (MPa)	47.59646	0.496	36.72802	3.267	28.94383	1.082

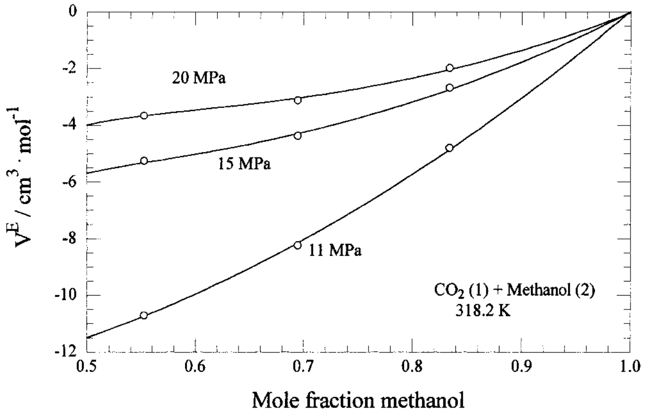

Figure 5. Excess molar volumes for the CO_2 (1) + methanol (2) system at 318.2 K; lines calculated from eq 4.

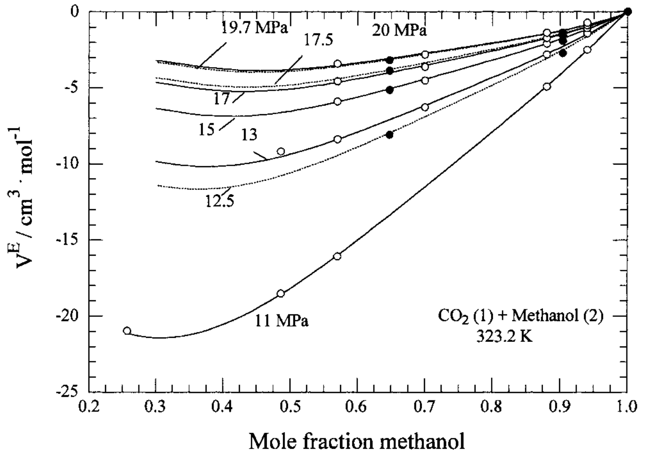

Figure 6. Excess molar volumes for the CO_2 (1) + methanol (2) system at 323.2 K; lines calculated from eq 4; white circles, this work; filled circles, Galicia-Luna et al.;[9,10] dashed lines calculated from eq 4 at the pressures of ref 9.

in this section was to provide a correlation for interpolation, *not extrapolation*, of the data, we combined the Redlich−Kister expansion with the Tait form of equation to give the set of empirical correlating equations,

$$B = x_1 B_1 + x_2 B_2 \tag{2}$$

$$V_0 = x_1 V_1 + x_2 V_2 + x_1 x_2 (A_1 + A_2(x_1 - x_2) + A_3(x_1 - x_2)^2) \tag{3}$$

$$V_{\mathrm{mix}} = V_0(1 - c \ln((B + P)/(B + P_0))) \tag{4}$$

where x_1 and x_2 are the mole fractions of carbon dioxide and methanol, respectively, and V_{mix} is the mixture molar volume. The V_1, V_2, B_1, B_2, A_1, A_2, and A_3 are empirical parameters determined by a least-squares fit of the $P-V$ data at a given temperature. The V_1 and V_2 should not be confused with the pure component molar volumes at the given temperature and pressure since eq 4 can only be applied over a limited composition range. The c and P_0 in eq 4 could have been used as fitting parameters, but in this work, we assigned values of c to be a constant independent of temperature and the reference pressure, P_0, to be 11 MPa, according to initial evaluations and parameter sensitivities. It should be noted that eq 4 cannot be extrapolated to the saturation region or to CO_2-rich mole fractions due to its functional form and choice of reference state, P_0 and V_0.

Fitted values for eq 4 are summarized in Table 4 and calculated deviations for each point are shown in Tables 1−3 with the average percent deviation of the correlation from the data for all data points being 0.08%. Percent deviations of the model versus the data are shown for each point in the tables. Parameter standard deviations were calculated and are given in Table 4 and can be used to calculate the 95% confidence interval of the parameters (not shown). Standard deviations of the A and V parameters were smaller compared with those of the B parameters and indicated a lower range of variability. Values of the covariance matrix indicated low correlation between the parameters. The χ^2 values (correlation coefficients) were 0.00984 (0.999968), 0.0363 (0.99988), and 0.3179 (0.99989) for the 318.2 K, 318.2 K, and 323.2 K data, respectively. Higher variability for the 323.2 K data set was probably due to the wider range of carbon dioxide mole fractions studied.

Comparison with Other Data. Several other researchers have reported densities of carbon dioxide + methanol mixtures as noted in the Introduction. Brunner et al.[20] measured densities along the CO_2 + methanol saturation curve with a static apparatus to a nominal precision of 2.5 digits whereas in this work densities in the compressed regions were measured and therefore these data cannot be directly compared. Roškar et al.[7] reported CO_2 + methanol molar volumes at 308.2 K, 323.2 K, and 338.2 K with a static apparatus to a nominal precision of 2.5 digits. However, the region of measurement of Roškar et al.[7] extends into the two-phase region of Brunner et al.,[20] indicating some inconsistency in the compositions reported, specifically, $x_2 = 0.571$ and $x_2 = 0.781$. The data of Goldfarb et al.[11] are mainly in the region of CO_2-rich mole fractions, where we have not made measurements and show excess volumes that are positive. The data set that we chose for comparison are the high-precision measurements of Galicia-Luna et al., who used a vibrating tube method.[9,10] The data applicable to our region of measurement are plotted in Figures 3−6 and calculations made with eq 4 at the compositions reported by those authors are shown by the dashed lines. Good agreement (0.25%) between the molar volumes of this work and those of the literature can be seen at the methanol mole fraction of 0.6476 but only fair agreement (0.8%) is apparent in the methanol mole fraction of 0.9039 and for one point at high CO_2 mole fractions at 12.5 MPa. The data are also compared in Figure 6, where experimental data and calculated excess molar volumes are shown. Good agreement can be seen between the two data sets.

Conclusions

We have reported density data for methanol + CO_2 mixtures, where methanol is in its expanded liquid state. The data should find use in the analyses of dielectric spectra data as well as in other fields related to liquid chromatography and gas antisolvent crystallization. A simple correlation equation was developed for interpolating within the conditions of measurement. Extreme caution should be used when extrapolating values, specifically, extrapolation to lower pressures or to higher carbon dioxide mole fractions. Extrapolation of the correlating equation to higher pressures, on the other hand, can probably provide acceptable results.

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