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PVT Relationships in a Carbon Dioxide-Rich Mixture with Ethane[1]

G. J. Sherman,[2] J. W. Magee,[2] and J. F. Ely[2]

Comprehensive isochoric *PVT* measurements have been obtained for the system ($0.99\ CO_2 + 0.01\ C_2H_6$). The range of state points studied includes those with densities from 2 to $24\ mol \cdot dm^{-3}$, temperatures from 245 to 400 K, and pressures to 35 MPa. Extensive comparisons have been made with two predictive conformal solution models, one which uses the 32-term BWR-type equation of Stewart and Jacobsen as a reference and the other using the newer Schmidt–Wagner functional form. Results obtained with the Schmidt–Wagner equation are better in the near-critical region owing to the flatter critical isotherm associated with this functional form.

KEY WORDS: carbon dioxide; corresponding states; ethane; mixture; *PVT* data.

1. INTRODUCTION

During the past 12 years, great interest has developed in the thermophysical properties of pure carbon dioxide and mixtures rich in carbon dioxide. This interest has evolved from several sources, most notably enhanced oil recovery using carbon dioxide and related CO_2 pipeline and CO_2-rich gas processing technologies. There also exist many potential applications for using carbon dioxide as a solvent in supercritical fluid extraction. Perhaps the most pressing need for thermophysical property data on CO_2-rich mixtures has arisen from the necessity of determining mass flow rates in carbon dioxide pipelines. Since carbon dioxide has a

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[2] Thermophysics Division, National Institute of Standards and Technology (formerly National Bureau of Standards), Boulder, Colorado 80303, U.S.A.

critical-point temperature which is close to ambient and since pipeline pressure is such that the fluid is only slightly supercritical, critical phenomena can play an important role in the transportation and custody transfer of CO_2-rich mixtures. For example, Chang et al. [1] have shown that small concentrations of impurities in a fluid can have great effects on the thermophysical properties of that fluid in the near-critical region. Since models cannot accurately predict thermophysical property behavior in this region, accurate experimental data are essential. Of the possible thermophysical property measurements, the *PVTx* relationship constitutes the most important property since an accurate and precise description of the *PVTx* surface can, in principle, be used to calculate the residual contribution to all other properties.

The most important impurities in pipeline carbon dioxide are methane, nitrogen, and ethane, and to a lesser extent, propane and heavier hydrocarbons. In previous communications we have reported the results of our *PVT* measurements for a mixture of $(0.98\, CO_2 + 0.02\, CH_4)$ [2] and a mixture of $(0.98\, CO_2 + 0.02\, N_2)$ [3]. In this paper we report the results of *PVT* measurements on the $(0.99\, CO_2 + 0.01\, C_2H_6)$ system. This system has been studied in more detail than other systems owing to the similarity of the components' critical states. Three previous *PVT* studies have been reported for this system [4–6], but none have reported measurements for compositions above 94 mol% carbon dioxide. In addition to the measurements, we have used these new data to evaluate a predictive corresponding-states model, DDMIX, which has been developed to represent the properties of carbon dioxide-rich mixtures.

2. EXPERIMENTAL

The *PVT* apparatus and methods used in this study have been described in detail elsewhere [2, 7] and are only summarized here. The apparatus consists of these principal components: a cylindrical copper cell (approx. 28 cm^3 internal volume), an oscillating quartz crystal pressure transducer, a platinum resistance thermometer, and a vacuum jacketed cryostat. Pressures are measured within ±0.01% using a transducer which has been calibrated with piston deadweight gauges. Temperatures are measured to better than 0.030 K with a 25-Ω platinum resistance thermometer using a $6\frac{1}{2}$ digit nanovoltmeter. All apparatus volumes were measured to within ±0.05% by using hydrogen gas expansions from a glass bulb whose volume had been calibrated by weighing with water. Sample masses are measured to ±0.002 g with a precision balance.

The CO_2 and C_2H_6 used in this study are research-grade gases. Chromatographic analyses showed the purity of these materials to be

0.999 946 for CO_2 and 0.999 89 for C_2H_6. The mixture was prepared gravimetrically in a thoroughly cleaned and dried aluminium cylinder. Weighings were performed with a double-pan 25-kg-capacity balance that had a certified standard deviation of 0.51 mg. The resulting composition of the mixture was 0.990 001 ± 0.000 06 mol fraction CO_2 and 0.009 999 ± 0.000 02 mol fraction C_2H_6.

The isochoric *PVT* method was used in this study. In this method, a sample of fixed mass is confined in a container of nearly constant volume. A sequence of pressures is measured at fixed increments of temperature until the upper limit of pressure or temperature is reached. Upon completion of a run, the sample is cryopumped from the cell into a weighing cylinder, and then the sample is weighed with a high-precision balance. The actual mass in the cell during each (P, T) observation is obtained by subtracting the computed amounts residing in the connecting capillaries and pressure transducer from the total mass. The contributions of all sources of error to the uncertainty of the density measurements lead to the conclusion that the densities are accurate to better than ±0.1 %.

3. EXPERIMENTAL RESULTS

A total of 13 isochores was investigated during this study with nominal densities ranging from 2 to 24 $\mathrm{mol \cdot dm^{-3}}$. Each isochore consisted of 5 to 10 points with temperatures ranging from 245 to 400 K. Pressures varied from 2.8 to 35.3 MPa. Table I lists the experimentally measured pressures as a function of density and temperature. The number of significant figures reported in Table I is a reflection of the precision rather than the absolute accuracy of the data. Isochores were closely spaced around the nominal critical density of this system ($\sim 10\ \mathrm{mol \cdot dm^{-3}}$), with isochore spacing being larger as the dense liquid and dilute gas states were approached. Each isochore was terminated when either the upper temperature (400 K) or the upper pressure (35 MPa) limit of the apparatus was reached.

4. EXTENDED CORRESPONDING-STATES MODEL

One of the most accurate models for predicting densities is based on the extended corresponding states theory. This theory was originally proposed by Leland and co-workers [8–10] and has been extensively applied to cryogenic systems [11, 12]. We have used this basic model in our studies on CO_2-rich mixtures owing to its success in predicting the density of liquefied natural gases [12, 13] and ethane–propane mixtures [14, 15], even relatively close to the critical point of the mixture. In

Table I. Experimental and Calculated *PVT* Relations for the (0.99 CO_2 + 0.01 C_2H_6) Mixture

T (K)	P (MPa)	Expt ρ ($mol \cdot dm^{-3}$)	MBWR ρ^a		SW ρ^b	
			$mol \cdot dm^{-3}$	%	$mol \cdot dm^{-3}$	%
270.000	3.1851	2.008	1.986	−1.06	1.990	−0.87
280.000	3.4285	2.006	1.998	−0.40	1.999	−0.34
300.000	3.8803	2.002	2.002	−0.01	2.002	−0.02
310.000	4.0932	2.001	2.000	−0.03	2.000	−0.05
320.000	4.3024	1.999	1.998	−0.04	1.997	−0.07
340.000	4.7123	1.995	1.995	0.00	1.994	0.06
360.000	5.1126	1.991	1.992	0.06	1.990	−0.04
380.000	5.5043	1.987	1.989	0.09	1.987	−0.03
400.000	5.8909	1.983	1.986	0.16	1.983	0.02
290.000	5.3418	4.002	3.924	−1.94	3.949	−1.33
300.000	5.9046	3.998	3.976	−0.55	3.985	−0.33
310.000	6.4237	3.990	3.975	−0.37	3.981	−0.21
320.000	6.9264	3.986	3.973	−0.32	3.979	−0.16
330.000	7.4123	3.981	3.967	−0.35	3.973	−0.21
340.000	7.8892	3.976	3.963	−0.33	3.968	−0.21
360.000	8.8200	3.967	3.958	−0.23	3.960	−0.16
380.000	9.7261	3.956	3.953	−0.08	3.952	−0.09
400.000	10.6103	3.943	3.946	0.07	3.943	−0.00
290.000	5.3310	3.962	3.903	−1.48	3.927	−0.88
300.000	5.8779	3.957	3.936	−0.53	3.945	−0.32
310.000	6.3982	3.950	3.935	−0.39	3.941	−0.23
320.000	6.8864	3.945	3.934	−0.30	3.939	−0.15
330.000	7.3677	3.941	3.929	−0.30	3.935	−0.16
340.000	7.8380	3.936	3.925	−0.30	3.930	−0.18
360.000	8.7589	3.927	3.920	−0.17	3.923	−0.11
380.000	9.6545	3.916	3.916	−0.01	3.915	−0.03
400.000	10.5269	3.904	3.909	0.12	3.906	0.04
300.000	6.7109	6.034	5.966	−1.13	5.989	−0.76
310.000	7.6121	6.027	6.007	−0.33	5.999	−0.45
320.000	8.4709	6.019	5.992	−0.45	5.995	−0.40
330.000	9.3037	6.010	5.979	−0.53	5.989	−0.35
340.000	10.1170	6.001	5.969	−0.54	5.983	−0.30
360.000	11.6980	5.980	5.954	−0.43	5.968	−0.19
380.000	13.2357	5.959	5.944	−0.25	5.954	−0.08
400.000	14.7396	5.941	5.934	−0.12	5.940	−0.02

[a] Calculated with the extended corresponding-states model with the MBWR-32 reference-fluid equation of state.

[b] Calculated with the extended corresponding states model with the Schmidt–Wagner reference-fluid equation of state.

Table I. *(Continued)*

T (K)	P (MPa)	Expt ρ ($mol \cdot dm^{-3}$)	MBWR ρ^a		SW ρ^b	
			$mol \cdot dm^{-3}$	%	$mol \cdot dm^{-3}$	%
310.000	8.2613	9.029	9.027	−0.03	8.950	−0.88
320.000	9.6842	9.015	8.990	−0.28	8.980	−0.39
330.000	11.0894	8.998	8.973	−0.29	8.982	−0.19
340.000	12.4721	8.980	8.950	−0.33	8.962	−0.20
360.000	15.2072	8.951	8.930	−0.24	8.928	−0.15
380.000	17.9069	8.930	8.917	−0.14	8.922	−0.08
400.000	20.5765	8.911	8.907	−0.04	8.912	0.01
310.000	8.1395	8.136	8.161	0.31	8.080	−0.69
320.000	9.3862	8.123	8.088	−0.44	8.067	−0.70
330.000	10.6150	8.109	8.071	−0.47	8.074	−0.44
340.000	11.8200	8.093	8.054	−0.48	8.056	−0.35
360.000	14.1809	8.065	8.030	−0.43	8.044	−0.26
380.000	16.4996	8.044	8.018	−0.32	8.029	−0.19
400.000	18.7853	8.026	8.009	−0.21	8.017	−0.11
310.000	8.2716	9.096	9.108	0.13	9.034	−0.68
320.000	9.7090	9.081	9.068	−0.15	9.061	−0.23
330.000	11.1249	9.064	9.041	−0.25	9.051	−0.15
340.000	12.5258	9.046	9.025	−0.23	9.037	−0.10
360.000	15.2881	9.017	9.000	−0.19	9.008	−0.10
380.000	18.0164	8.995	8.986	−0.10	8.991	−0.05
400.000	20.7078	8.977	8.972	−0.06	8.976	−0.01
310.000	8.3827	10.131	10.019	−1.11	10.018	−1.12
320.000	10.0205	10.114	10.059	−0.55	10.090	−0.24
330.000	11.6546	10.094	10.062	−0.32	10.086	−0.08
340.000	13.2785	10.074	10.052	−0.22	10.065	−0.08
360.000	16.5067	10.044	10.032	−0.12	10.032	−0.12
380.000	19.7076	10.022	10.014	−0.08	10.010	−0.12
400.000	22.8822	10.002	9.998	−0.05	9.995	−0.07
310.000	8.4983	11.202	10.957	−2.18	11.062	−1.25
320.000	10.3650	11.182	11.097	−0.76	11.164	−0.17
330.000	12.2469	11.159	11.127	−0.27	11.156	−0.01
340.000	14.1298	11.137	11.127	−0.09	11.133	−0.03
360.000	17.8935	11.108	11.108	0.00	11.097	−0.10
380.000	21.6474	11.085	11.088	0.02	11.074	−0.09
310.000	8.6192	12.142	11.813	−2.70	11.971	−1.40
320.000	10.7140	12.120	12.012	−0.89	12.076	−0.36
330.000	12.8400	12.093	12.056	−0.30	12.069	−0.20
340.000	14.9806	12.072	12.065	−0.06	12.053	−0.15
360.000	19.2805	12.042	12.051	0.07	12.027	−0.12

Table I. *(Continued)*

T (K)	P (MPa)	Expt ρ (mol·dm^{-3})	MBWR ρ^a		SW ρ^b	
			mol·dm^{-3}	%	mol·dm^{-3}	%
300.000	7.2492	16.089	16.070	−0.11	16.058	−0.19
310.000	10.7535	16.057	16.053	−0.02	16.039	−0.11
320.000	14.3327	16.018	16.029	0.06	15.999	−0.11
330.000	17.9694	15.993	16.007	0.08	15.974	−0.12
340.000	21.6373	15.975	15.985	0.06	15.955	−0.12
280.000	5.7730	20.294	20.295	−0.01	20.293	0.00
285.000	8.9746	20.269	20.268	0.00	20.266	−0.01
290.000	12.1560	20.236	20.237	0.01	20.236	0.00
295.000	15.3304	20.208	20.207	−0.01	20.207	−0.01
300.000	18.5546	20.191	20.187	−0.02	20.188	−0.01
305.000	21.7949	20.177	20.169	−0.04	20.173	−0.02
310.000	25.0451	20.165	20.154	−0.05	20.161	−0.02
315.000	28.3032	20.154	20.141	−0.06	20.150	−0.02
320.000	31.5463	20.143	20.127	−0.08	20.139	−0.02
325.000	34.7931	20.133	20.115	−0.09	20.129	−0.02
245.000	2.7934	24.165	24.145	−0.08	24.153	−0.05
250.000	8.2664	24.133	24.114	−0.08	24.115	−0.07
255.000	13.5008	24.083	24.070	−0.06	24.066	−0.07
260.000	18.8567	24.053	24.040	−0.06	24.033	−0.08
270.000	29.8514	24.019	24.010	−0.04	23.999	−0.08

addition, this type of model allows for the direct incorporation of pure-component PVT data via exact shape factors, thereby minimizing the errors in mixture prediction associated with the pure fluid limits.

From an applied point of view, the theory tells us that the dimensionless residual Helmholtz energy and the compressibility factor of a mixture are related to those of a pure reference fluid by

$$a_x^r(V_x, T_x) = a_o^r(V_o, T_o) \tag{1}$$

and

$$Z_x^r(V_x, T_x) = Z_o^r(V_o, T_o) \tag{2}$$

In Eq. (1), $a^r = [A(V, T) - A^*(V, T)]/RT$, where A is a Helmholtz free energy, the asterisk indicates an ideal-gas value, R is the gas constant, and T is the absolute temperature. The subscript x indicates the mixture or a pure fluid and o indicates a reference fluid whose thermodynamic properties are known, in principle, with great accuracy. Z^r is the residual compressibility factor, $Z-1$. The arguments which lead to Eqs. (1) and (2) provide a relation between the volume and the temperature of the fluid x and the corresponding values for the reference fluid,

$$T_o = T_x/f_x \qquad \text{and} \qquad V_o = V_x/h_x$$

The scale factors f_x and h_x are called the equivalent substance reducing ratios. In extended corresponding-states theory between two pure fluids, they are given by

$$f_j = (T_j^c/T_o^c)\,\Theta_{jo}(\rho, T) \tag{3}$$

and

$$h_j = (V_j^c/V_o^c)\,\Phi_{jo}(\rho, T) \tag{4}$$

where the superscript c denotes a critical-point parameter and Θ and Φ are called shape factors. The density and temperature dependence of the shape factors enable us to force two pure fluids to obey corresponding states exactly.

In early applications of the extended corresponding-states model generalized formulas [9] were used for the shape factors appearing in Eqs. (3) and (4). When those formulas were developed, high-accuracy equations of state and broadly based experimental data for homologous series were not available. It was decided, therefore, at the inception of this work that recent pure fluid experimental data should be correlated and exact shape factors should be calculated and used in the mixture calculations. This approach will lead to a mixture model which will have essentially no uncertainties in the pure component limit.

The shape factors (or equivalently f_j and h_j) are obtained by simultaneously solving the corresponding-states relations Eqs. (1) and (2) for f_j and h_j for each component. In order to perform these calculations, high-accuracy representations of the *PVT* surfaces for the mixture components and the reference fluid are required. Since a large number of fluid *PVT* surfaces had previously been represented with the 32-term BWR type equation proposed by Jacobsen and Stewart [16], it was decided to retain that functional form in the shape factor calculations and subsequent mixture investigations. The coefficients for this equation of state have been determined for eight fluids: methane [17], ethane [17], propane [17], *i*-butane [17], *n*-butane [17], carbon dioxide [3, 18], carbon monoxide, and hydrogen sulfide. In addition, previous work has provided equation of state coefficients for nitrogen [19], oxygen [19], argon [19], and ethylene [20]. Thus, high-accuracy equations of state by which shape factors can be calculated have been obtained for 12 fluids.

Once the shape factors are available, mixture calculations may be performed by using mixing and combining rules to find the equivalent substance reducing ratios for the mixture, *viz.*,

$$h_x = \sum \sum x_i x_j h_{ij}$$

and

$$f_x h_x = \sum \sum x_i x_j f_{ij} h_{ij}$$

where the cross terms are obtained from the combining rules

$$f_{ij} = (f_i f_j)^{1/2} (1 - k_{ij})$$

and

$$h_{ij} = \tfrac{1}{8}(h_i^{1/3} + h_j^{1/3})(1 - l_{ij})$$

k_{ij} and l_{ij} are the normal binary interaction parameters.

4.1. Application to the $CO_2 + C_2H_6$ Binary Mixture

A computer program, DDMIX, which incorporates the extended corresponding-states model was constructed. Propane was used as the

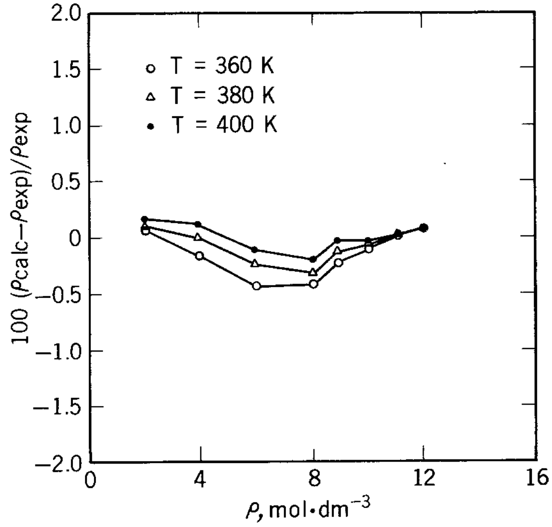

Fig. 1. Comparison of the experimental and calculated densities using DDMIX for the $CO_2 + C_2H_6$ system at 360, 380, and 400 K.

reference fluid in the model owing to its low reduced triple-point temperature. Binary interaction parameters for the $CO_2 + C_2H_6$ binary were optimized using the *PVT* data of Reamer et al. [4]. The optimal values were found to be $k_{ij} = 0.0949$ and $l_{ij} = -0.0316$. From these values and the shape factors and mixing rules described above, densities were predicted given the experimental temperatures and pressures. The predicted values are listed in Table I along with the percentage deviations. Figures 1–3 summarize these deviations along isotherms. In general the agreement is good—the rms deviation in density is 0.47% and has a bias of −0.28%. Some of the bias could be removed by optimizing the interaction parameters with the new data.

In spite of the good results obtained with the model, the predicted near-critical isotherms exhibit systematic differences from the experimental measurements. This is especially evident in Fig. 3 for the 310 K isotherm, which is roughly 6 K above the critical temperature. The deviation pattern observed is similar to that obtained with a pure fluid equation of state which is not flat enough in the supercritical region, i.e., predicted densities are too high at less than the critical density and too low at points greater than the critical density. Of the three elements which went into the predictive model (shape factors, mixing rules, and reference-fluid equation of

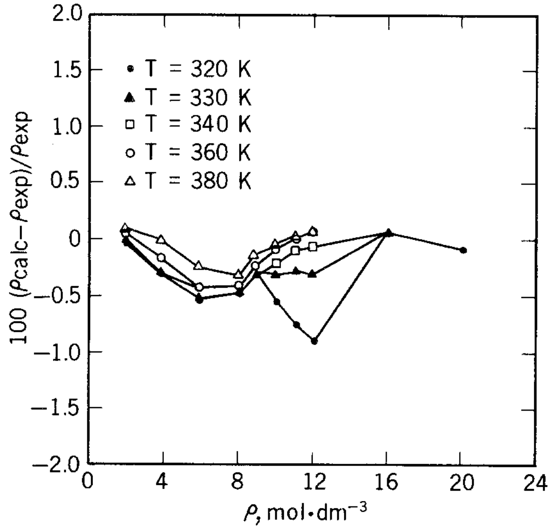

Fig. 2. Comparison of the experimental and calculated densities using DDMIX for the $CO_2 + C_2H_6$ system in the temperature range 320 to 380 K.

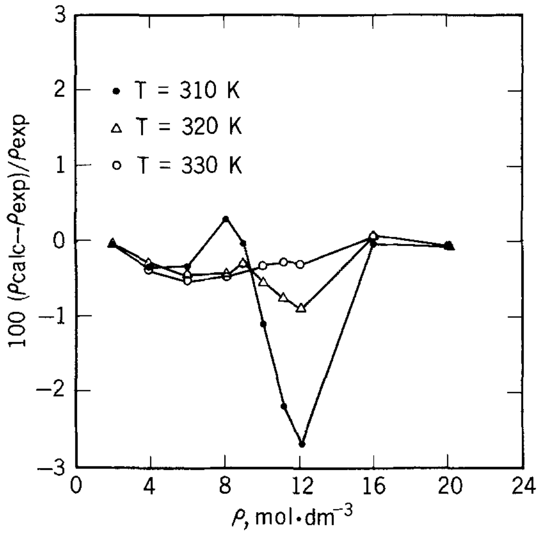

Fig. 3. Comparison of the experimental and calculated densities using DDMIX for the $CO_2 + C_2H_6$ system at 310, 320, and 330 K.

state), the systematic error most likely arises from the latter. We decided to explore, therefore, another reference-fluid equation of state which had a flatter critical region.

4.2. Schmidt–Wagner Reference Fluid

In 1985 Schmidt and Wagner (SW) [21] proposed a type equation of state for oxygen which is flatter in the critical region. This flatness is achieved by using two exponential terms rather than the one that is common to BWR-type equations. We have fit this equation to the thermodynamic surfaces of four fluids (carbon dioxide [18, 22], methane [23], ethane, and propane). Given these equations, we developed a hybrid corresponding-states program capable of using either the 32-term MBWR or the SW functional form for a given component and calculated the *PVT* data of the carbon dioxide + ethane system reported here. The results are also listed in Table I along with the observed percentage deviations. In general there is no difference between the results obtained with the two models except in the near-critical region, where the SW reference fluid provides much improved results. This is shown in Figs. 4 and 5, which compare the results obtained with the two models for the 310 and 320 K isotherms. The improvement is dramatic, especially on the 310 K isotherm.

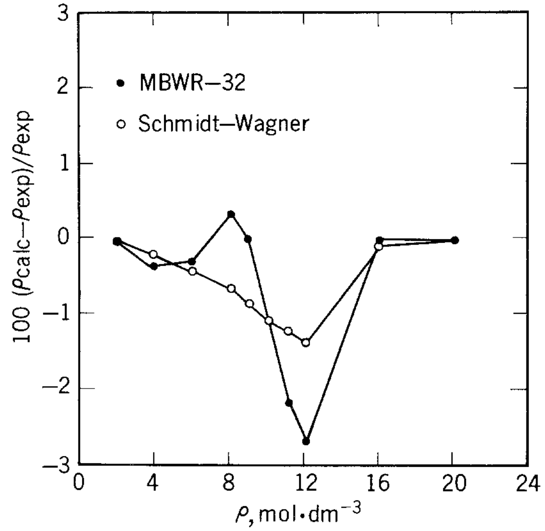

Fig. 4. Comparison of the density deviations obtained with DDMIX and those obtained with the Schmidt–Wagner equation of state as the reference fluid at 310 K.

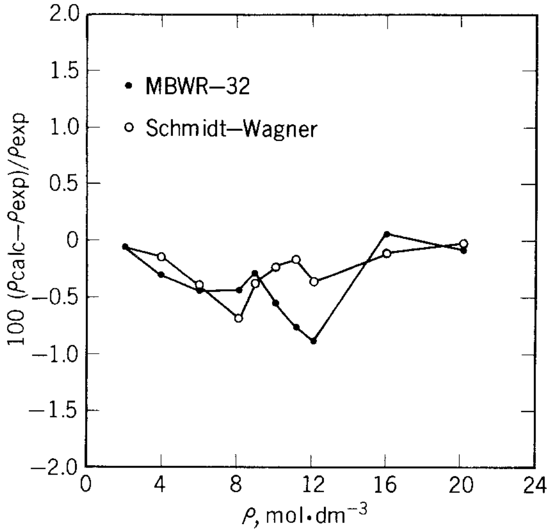

Fig. 5. Comparison of the density deviations obtained with DDMIX and those obtained with the Schmidt–Wagner equation of state as the reference fluit at 320 K.

The overall results obtained with the SW-based model are also good, i.e., a rms density deviation of 0.30% with a bias of −0.23%. Again, some of the bias may be removed by refitting the binary interaction parameters.

5. SUMMARY AND CONCLUSIONS

We have reported the results of extensive *PVT* measurements for the $(0.99\,CO_2 + 0.01\,C_2H_6)$ binary mixture. Comparisons of the data with a predictive extended corresponding-states computer model were very good. It was observed, however, that one needs to improve the corresponding-states reference fluid behavior in the near-critical region to obtain predictions which are comparable to the experimental accuracy. Use of the Schmidt–Wagner formulation was a step in this direction—future work may include using a rescaled equation of state such as that of Erickson et al. [25] in that role.

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