(4) Montgomery, J. B.; DeVries, T. *J. Am. Chem. Soc.* **1942**, *64*, 2375.
(5) Yaws, C. L. "Physical Properties"; McGraw-Hill: New York, 1977.
(6) "Preparation of the Coal Conversion Data Book"; Institute of Gas Technology: Chicago, IL, 1981; report to Department of Energy, Project No. 61003, pp I-32, I-41.
(7) "Selected Values of Properties of Hydrocarbons and Related Compounds"; Thermodynamics Research Center Hydrocarbon Project, Thermodynamics Research Center, Texas A&M University: College Station, TX, 1972 (loose-leaf data sheets, extant).
(8) Eubank, P. T.; Holste, J. C.; Cediel, L. E.; Moor, D. H.; Hall, K. R. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 105.
(9) Cediel, L. E.; Ph.D. Dissertation, Department of Chemical Engineering, Texas A&M University, College Station, TX, 1983.
(10) Ambrose, D. "Vapour-Liquid Critical Properties"; National Physical Laboratory Report Chem. 107: Teddington, Middlesex, U.K., 1980.
(11) Zwolinski, B. J.; Wilhoit, R. C. "Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds"; API44-TRC Publications in Science and Engineering, No. 101: College Station, TX, 1971.

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Densities and Viscosities of Mixtures of Carbon Dioxide and *n*-Decane from 310 to 403 K and 7 to 30 MPa

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Experimental measurements of densities and viscosities of compressed fluid mixtures of carbon dioxide and *n*-decane are reported for temperatures between 310 and 403 K and pressures between 7 and 35 MPa. The estimated uncertainty in the density data is 0.5 kg/m^3 and that of the viscosity data is 2%. The measured fluid densities and viscosities are compared with values predicted by the principle of corresponding states. The predictions are significantly improved by using binary interaction coefficients in the mixing rules for the equivalent substance-reducing ratios.

Introduction

The use of carbon dioxide in enhanced oil recovery has caused an increased interest in the fluid property behavior of carbon dioxide/hydrocarbon mixtures. Phase compositions, densities, viscosities, and interfacial tensions of carbon dioxide/hydrocarbon mixtures must be known for accurate simulation of carbon dioxide displacement processes. The development of methods for predicting fluid properties of these mixtures depends on the availability of good experimental data. Although phase behavior of carbon dioxide/hydrocarbon binary mixtures has been widely reported (see the bibliography of ref *1*), densities and viscosities of these fluids have generally not been measured.

Reamer and Sage (*2*) reported the phase behavior and phase molar volumes along the saturation boundaries for carbon dioxide/*n*-decane mixtures. We report measurements of densities and viscosities of carbon dioxide/*n*-decane mixtures above their bubble point pressures. Temperatures range from 310 to 403 K, and pressures range from 7 to 35 MPa. We also test the capability of the extended corresponding states program TRAPP (*3*) to predict densities and viscosities of these mixtures. By use of binary interaction coefficients in the corresponding states mixing rules, the predictions are significantly improved.

Experimental Section

Materials. Nitrogen and carbon dioxide were obtained from Welder's Supply and have nominal purities of 99.995% and 99.999%, respectively. Water was triple-distilled and was degassed prior to use. Nitrogen and water were used to calibrate the densimeter as described below. *n*-Decane was Phillips Petroleum 99.1 mol % nominal purity and was degassed prior to use.

Apparatus. A schematic diagram of the apparatus appears as Figure 1. The two pressure vessels and 1 and 2 are made of 316 stainless steel and are rated to 41 MPa at 410 K. Each vessel contains a floating piston which separates mercury pressure fluid from the experimental fluid. The maximum fluid volume of each vessel is approximately 200 cm^3. The pump (PDP) is a Ruska Instruments Inc. piston drive pump. The pump drives compessed fluid from vessel 1 through the viscometer (CT) and densimeter (D) into vessel 2. Pressure is regulated by a diaphragm back-pressure regulator with nitrogen as a pressure buffer.

The constant-temperature bath is a forced-air oven with a 2800-W heater. The heater power is controlled proportionally with a Valco Instruments Co., Inc., instrumentation temperature controller which uses a type E thermocouple as sensor. Temperature at a given location in the oven remains stable to within 0.02 K for several hours at a time. The maximum temperature gradient across the oven was measured as 0.3 K.

Specific mixture concentrations of *n*-decane and carbon dioxide were introduced into the apparatus by measuring specified volumes of the components from supply vessels 3 and 4. The density of *n*-decane was measured at the conditions of the supply vessel in the densimeter described below. The density of carbon dioxide at its supply conditions was calculated by using the IUPAC carbon dioxide equation at state (*4*).

Complete mixing of the two components was achieved by flowing the fluid rapidly back and forth between vessels 1 and 2 while simultaneously stirring the fluid remaining in vessel 1 with a magnetic rotator.

Temperature Measurement. A set of thre type E thermocouples, nickel–chromium alloy vs. copper–nickel alloy (chromel–constantan), was used for temperature measurement. The thermocouples were calibrated against a Leeds and Northup platinum resistance thermometer whose resistance was measured by using a Leeds and Northup potentiometric Mueller bridge with mercury contacts and a Keithly null microvoltmeter. The platinum resistance thermometer was calibrated at the U.S. National Bureau of Standards (*5*). The estimated uncertainty in temperature determination is estimated to be ±0.03 K, based on the International Practical Temperature Scale-68.

One thermocouple was inserted into the densimeter thermocouple well, as described below. A second thermocouple was attached to vessel 1, and the third thermocouple was at-

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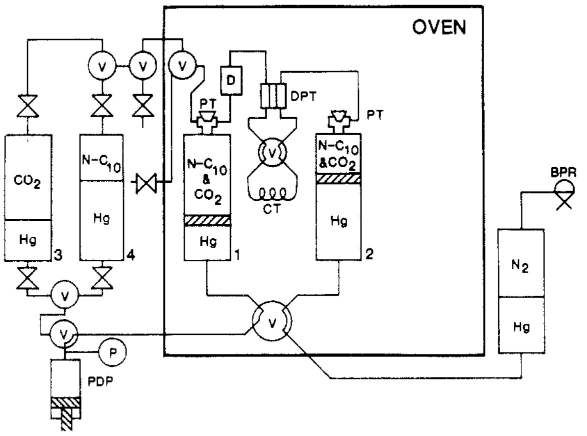

Figure 1. Density and viscosity apparatus: (Hg) mercury, (PDP) positive displacement pump, (D) Mettlar/Paar DMA512 densimeter cell, (V) valves, (1–4) high-pressure vessels, (BPR) back-pressure regulator, (DPT) differential pressure transducer, (PT) pressure transducer, (P) heise pressure gauge, (CT) capillary tube.

tached to the capillary tube viscometer.

Pressure Measurement. Absolute pressures were measured with a Heise gauge calibrated to 0.1% accuracy against a Chandler Engineering dead-weight tester. Absolute pressures were also monitored at vessels 1 and 2 by calibrated Sensotec Model A-205 pressure transducers.

Differential pressures across the capillary viscometer were measured with a Sensotec Model A-5 wet/wet differential pressure transducer, which has a line pressure rate of 34.5 MPa. The transducer was calibrated against the dead-weight gauge at static conditions to ±0.3-kPa accuracy between 0- and 345-kPa differential pressure. Transducer output is read on Sensotec Model SA-10D multifunctional digital indicator, which outputs a voltage signal that is recorded on a pen chart recorder. Under flowing conditions, the average of the combined repeatability and precision of the pressure reading on the differential transducer is estimated as 0.9 kPa.

Density Measurement. The densimeter consists of a Mettler/Paar DMA512 high-pressure cell and a Mettler/Paar DMA60 seven-digit frequency counter. The DMA512 contains a U-shaped stainless steel tube which has 1-cm^3 volume. The cell is fused into a double-walled cylidner through which a thermostated fluid can be circulated. There is a cavity surrounding the sample cell which is filled with a high thermal conductivity gas and which contains a capillary tube thermocouple well. The measuring principle of the densimeter has been described previously (*6*). The densimeter was calibrated by using distilled water and nitrogen as calibration substances, as done previously (*6*), to obtain correlations for the instrument k factors and water oscillation periods as functions of pressure and temperature.

Calibration measurements were made at 3.45-MPa intervals in the range of 3.45–34.5 MPa, and at 30 K intervals between 305 and 390 K. During the calibration measurements, temperature was controlled to within ±0.01 K by using an Exacal EX-100UHP constant-temperature circulating bath which circulated ethylene glycol through the cylinder containing the sample cell. Instrument k factors and the oscillation periods for water were fitted to functions of temperature and pressure to obtain two correlations, in a manner similar to that used previously (*6*). The correlations reproduced the measured data to an average absolute deviation of 0.05% for the instrument k factor and 0.01% for the water oscillation periods. The estimated uncertainty in density measurement is 0.5 kg/m^3.

Densities of n-decane and carbon dioxide were measured and compared with literature values. The densities of carbon dioxide were measured at four pressures between 7 and 34.5 MPa at each of five temperatures between 273 and 310 K. The average absolute deviation of the measured densities and densities calculated from the IUPAC equation of state (*4*) was 1.4 kg/m^3, which compares to the average uncertainty of the IUPAC predictions themselves with respect to experimental data of 1.5 kg/m^3. Densities of n-decane were also measured at two temperatures. These results appear in Table I, in which the measured densities from this work are compared with those of Sage, Lavender, and Lacey (*7*), who measured densities of a decane sample which contained some decane isomers. They are also compared with predicted by the TRAPP (*3*) computer program and by the COSTALD (*8*) method.

Table I. Densities of Decane

T = 310.94 K

	density, kg/m^3	
	7.10 MPa	20.64 MPa
this work (n-decane)	723.2	733.7
Sage (decane)[a]	725.8 ± 1.5	737.6 ± 1.5
Sage (cor)[b]	721.5	733.2
TRAPP[c]	725.3	733.8

T = 303.56 K

	density, kg/m^3	
	6.89 MPa	13.79 MPa
this work	728	733
TRAPP[c]	731	736
COSTALD[d,e]	728	733

[a] Reference *7*. [b] Measured density for decane sample reduced by 0.6% for the difference between decane and n-decane, as measured by Shepard et al. (*13*). [c] Reference *3*. [d] A correction for pressure has been added to the density at saturation pressure obtained from COSTALD. [e] Reference *8*.

Table II. Density and Viscosity of Binary Mixture of 0.850 Mole Fraction n-Decane and 0.150 Mole Fraction Carbon Dioxide

press., MPa	temp, K	density, kg/m^3	temp, K	viscosity, 10^{-6} Pa·s
6.93	310.93	728.1	310.91	666.6
14.06		734.1		704.5
20.81		739.9		752.7
28.37		745.0		812.3
34.63		749.3		864.7
6.72	344.32	701.5	344.33	446.2
14.17		709.5		484.1
20.89		716.1		516.
27.89		722.1		558.8
34.58		726.9		587.7
7.10	373.13	678.3	373.15	333.6
13.96		687.4		371.5
21.06		694.9		399.8
27.75		702.3		432.3
34.68		708.1		464.6
7.19	403.08	652.4	403.22	269.5
14.48		665.6		292.3
21.30		675.6		318.2
27.96		683.7		342.6
34.06		690.4		363.7

Viscometer. The viscometer consists of a stainless steel capillary tube and the Sensotec differential pressure transducer. The tube is 731.25 cm long and has a diameter of 0.032 69 ± 0.000 06 cm. The tube diameter was determined by measuring the pressure drop obtained when flowing n-decane through the tube at an inlet pressure of 6.89 and 20.68 MPa at 310.94 K. The experimental data of Carmichael et al. (*9*) were used, along with the measured pressure drop and known flow rate in the Hagen–Poulseille equation (*10*) to determine the tube diameter. Carmichael et al. (*9*) report an uncertainty of 5.8 × 10^{-6} Pa·s in the data used for these calibrations. Experimental flow rates range dfrom 16 to 64 cm^3/h for which the system exhibited

Table III. Density and Viscosity of Binary Mixture of 0.699 Mole Fraction n-Decane and 0.301 Mole fraction Carbon Dioxide

press., MPa	temp, K	density, kg/m^3	temp, K	viscosity, 10^{-6} Pa·s
7.16	310.92	735.1	310.90	547.1
14.28		740.9		589.2
21.06		746.9		629.8
27.72		752.9		669.9
34.09		757.8		709.9
7.02	344.31	704.4	344.31	388.7
14.13		712.7		413.7
20.86		720.2		442.9
27.83		727.4		476.3
34.51		733.1		506.1
6.76	374.01	676.7	374.02	288.1
13.72		687.5		309.5
20.99		697.4		339.3
27.75		705.1		366.1
33.96		711.9		390.5
7.10	403.08	650.08	403.22	225.8
14.24		664.4		246.0
20.86		675.8		271.3
27.78		685.6		291.4
33.89		693.3		308.6

Table IV. Density and Viscosity of Binary Mixture of 0.495 Mole Fraction n-Decane and 0.505 Mole Fraction Carbon Dioxide

press., MPa	temp, K	density, kg/m^3	temp, K	viscosity, 10^{-6} Pa·s
7.12	311.25	750.5	311.21	360.1
13.87		758.9		393.5
20.61		766.9		420.0
27.65		774.6		447.7
30.94		778.0		464.0
6.93	343.14	712.9	343.18	289.3
13.63		724.7		286.6
20.54		735.4		325.5
27.58		744.6		333.6
10.60	373.20	685.4	373.36	212.9
13.82		692.7		222.2
20.23		705.2		243.0
27.75		717.2		266.1
11.58	402.94	652.8	403.30	169.2
13.91		659.0		174.9
21.37		677.9		199.0
27.99		691.1		215.3

Table V. Density and Viscosity of Binary Mixture of 0.351 Mole Fraction n-Decane and 0.649 Mole Fraction Carbon Dioxide

press., MPa	temp, K	density, kg/m^3	temp, K	viscosity, 10^{-6} Pa·s
8.72	312.46	774.4	312.41	138.8
13.68		795.8		148.4
20.65		818.1		161.1
27.75		836.8		174.6
13.30	345.12	695.7	345.17	98.2
20.54		745.4		118.0
27.76		775.1		133.7
17.20	373.70	641.3	373.85	95.7
22.06		682.5		106.3
28.03		716.7		118.3
19.23	402.80	571.6	403.14	93.7
23.30		618.8		105.5
27.54		651.4		116.0

Table VI. Density and Viscosity of Binary Mixture of 0.150 Mole Fraction n-Decane and 0.850 Mole Fraction Carbon Dioxide

press., MPa	temp, K	density, kg/m^3	temp, K	viscosity, 10^{-6} Pa·s
8.72	312.46	774.4	312.41	138.8
13.68		795.8		148.4
20.65		818.1		161.1
27.75		836.8		174.6
13.30	345.12	695.7	345.17	98.2
20.54		745.4		118.0
27.76		775.1		133.7
17.20	373.70	641.3	373.85	95.7
22.06	682.5			106.3
28.03		716.7		118.3
19.23	402.80	571.6	403.14	93.7
23.30		618.8		105.5
27.54		651.4		116.0

Table VII. Comparison of Experimental and Calculated (TRAPP) Densities

temp, K	(±)AAD[a]	
	as interactn coeff[b]	with interactn coeff[c]
	0.150 Mole Fraction CO$_2$	
310.93	(−)3.79	(−)0.26
344.32	(−)3.52	(−)0.12
373.13	(−)3.33	(+)0.33
403.08	(−)2.93	(+)0.80
	0.301 Mole Fraction CO$_2$	
310.92	(−)7.69	(−)0.42
344.31	(−)7.52	(−)0.20
374.01	(−)7.24	(+)0.34
403.08	(−)6.71	(+)1.03
	0.505 Mole Fraction CO$_2$	
311.25	(−)12.1	(−)0.12
343.14	(−)12.2	(+)0.48
373.20	(−)12.1	(+)1.02
402.94	(−)12.0	(+)1.60
	0.649 Mole Fraction CO$_2$	
312.46	(−)15.5	(−)0.35
345.12	(−)15.6	(+)0.33
373.52	(−)16.0	(+)0.64
402.77	(−)15.8	(+)1.29
	0.850 Mole Fraction CO$_2$	
312.46	(−)17.0	(−)1.49
345.12	(−)19.1	(−)2.27
373.70	(−)20.7	(−)2.51
402.80	(−)22.7	(−)2.73

[a] Average absolute percent deviation: $100(\sum_{i=1}^{N}[|\text{experimental density} - \text{TRAPP density}|/\text{experimental density}]/N)$, where N is the number of data on the isotherm. (±) indicates the sign of the average percentage deviation. [b] TRAPP with interaction parameters of 0.0. [c] TRAPP with interaction parameters of $k_{ij} = 0.15$ and $l_{ij} = -0.2$.

laminar flow. Reynolds numbers were less than 0.03, and the calculated end effects for the tube were less than 10^{-9} Pa·s. The measured pressure differences across the tube for experimental viscosity determinations ranged from 29 to 310 kPa. Accounting for the uncertainty in the tube calibration arising from Carmichael's data and the uncertainty estimated for viscosity determinations is 2%.

Results

Tables II–VI present the density and viscosity data for carbon dioxide/n-decane mixtures for concentrations of 0.85 mole fraction n-decane to 0.15 mole fraction n-decane. All data were obtained above the mixture bubble point pressures (*2*). The estimated uncertainty in the densities is 0.5 kg/m^3 and in viscosities is 2%. The density uncertainties increase from approximately 0.07% of the density for 0.85 mole fraction n-decane to approximately 0.09% for 0.15 mole fraction n-decane.

Table VIII. Comparison of Experimental and Calculated (TRAPP) Viscosities

temp, K	(±)AAD[a,b]	(±)AAD[a,c]
	0.150 Mole Fraction CO_2	
310.91	(-)7.2	(+)5.2
344.33	(-)13.4	(-)0.9
373.17	(-)15.4	(-)3.0
403.22	(-)15.9	(-)3.9
	0.301 Mole Fraction CO_2	
310.90	(-)18.8	(+)6.3
344.31	(-)23.4	(+)2.0
374.02	(-)27.8	(-)1.6
403.22	(-)29.9	(-)3.6
	0.505 Mole Fraction CO_2	
311.21	(-)51.4	(-)3.8
343.18	(-)50.7	(-)4.6
373.36	(-)56.7	(-)7.9
403.30	(-)57.4	(-)9.0
	0.650 Mole Fraction CO_2	
312.42	(-)6.8	(-)8.4
345.14	(-)87.5	(-)20.9
373.67	(-)78.8	(-)15.8
403.11	(-)72.1	(-)12.8
	0.850 Mole Fraction CO_2	
312.41	(-)81.6	(-)26.3
345.17	(-)85.6	(-)30.1
373.85	(-)60.0	(-)13.8
403.14	(-)27.4	(+)8.3

[a] Average absolute percent deviation: $100(\sum_{i=1}^{N}[|\text{experimental viscosity} - \text{TRAPP viscosity}|/\text{experimental viscosity}]/N)$, where N is the number of data on the isotherm. (±) indicates the sign of the average percentage deviation. [b] TRAPP with interaction parameters of 0.0. [c] TRAPP with interaction parameters of $k_{ij} = 0.15$ and $l_{ij} = -0.2$.

Discussion of Property Predictions Using TRAPP

Calculations of the compressed-fluid properties were performed by using the principle of extended corresponding states (*11*) with Ely and Hanley's extended corresponding states computer program TRAPP (*3*). The results of these predictions are presented in Tables VII and VIII, in which each deviation represents an average over the data for an isotherm. TRAPP predictions for pure fluid *n*-decane and carbon dioxide are excellent (*3*). For the mixtures, however, the predictions are generally not good, particularly at high carbon dioxide concentrations. The average absolute percentage deviation for predicted densities is 11.7%, and for predicted viscosities it is 46.5%.

The mixture equivalent substance-reducing ratios ($f_{x,0}$;$h_{x,0}$) in the extended corresponding states formalism are presented in eq 21–26 in Ely and Hanley's paper (*3*) and are defined by the following mixing rules:

$$f_{x,0} = h_{x,0}^{-1} \sum_{\alpha}\sum_{\beta} x_{\alpha} x_{\beta} f_{\alpha\beta,0} h_{\alpha\beta,0}$$

$$h_{x,0} = \sum_{\alpha}\sum_{\beta} x_{\alpha} x_{\beta} h_{\alpha\beta,0}$$

where x_{α} is the mole fraction of pure fluid α. The binary factors $f_{\alpha\beta,0}$ and $h_{\alpha\beta,0}$ are defined by the following combining rules:

$$f_{\alpha\beta,0} = (f_{\alpha,0} f_{\beta,0})^{1/2}(1 - k_{\alpha\beta})$$

$$h_{\alpha\beta,0} = \tfrac{1}{8}\,(h_{\alpha,0}^{1/3} + h_{\beta,0}^{1/3})^{3}(1 - l_{\alpha\beta})$$

where $f_{\alpha,0}$ and $h_{\alpha,0}$ are pure fluid equivalent substance-reducing ratios and $k_{\alpha\beta}$ and $l_{\alpha\beta}$ are binary interaction parameters.

Ely and Hanley (*3*, *11*) set the binary interaction parameters equal to zero. Density and viscosity predictions for hydrocarbon mixtures do not appear to be very sensitive to the numerical values of the binary interaction parameters (*11*, *12*). However, for carbon dioxide/hydrocarbon binary mixtures, density and viscosity predictions are quite sensitive to the values of the binary parameters. Values for $k_{\alpha\beta}$ and $l_{\alpha\beta}$ for carbon dioxide/propane have been reported as 0.097 and -0.097, respectively, and for carbon dioxide/*n*-butane as 0.140 and -0.060, respectively (*12*). We determined optimal values for $k_{\alpha\beta}$ and $l_{\alpha\beta}$ for the carbon dioxide/*n*-decane binary mixtures to improve agreement between predicted and experimental densities of the carbon dioxide/*n*-decane mixtures. The optimal values of the interaction parameters are 0.15 for $k_{\alpha\beta}$ and -0.2 for $l_{\alpha\beta}$. By use of these parameters in the corresponding states mixing rules, the average absolute percentage deviation of the predicted densities is reduced from 11.7 to 0.9% (Table VII), and that of the predicted viscosities is reduced from 46.5% to 9.4% (Table VIII).

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Registry No. CO_2, 124-38-9; decane, 124-18-5.

Literature Cited

(1) Turek, Edward A.; Metcalfe, Robert S.; Yarbrough, Lyman; Robinson, Robert L. "Proceedings of the Society of Petroleum Engineers Fall Conference, Dallas, TX, Sept 21–24, 1980"; SPE paper no. 9231.
(2) Reamer, H. H.; Sage, B. H. *J. Chem. Eng. Data* **1963**, *8*, 508.
(3) Ely, James F.; Hanley, H. J. M. "Proceedings of the 60th Annual Convention of the Gas Processors Association, San Antonio, TX, March 23–25, 1981".
(4) Angus, S, de Reuck, K. M., Armstrong, B., Eds. "International Thermodynamic Tables of the Fluid State-3, Carbon Dioxide"; Pergamon Press: Oxford, 1976.
(5) Scheloske, J. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1981.
(6) Cullick, Alvin S.; Ely, James F. *J. Chem. Eng. Data* **1982**, *27*, 276.
(7) Sage, B. H.; Lavender, H. M.; Lacey, W. N. *Ind. Eng. Chem.* **1940**, *32*, 743.
(8) Hankinson, Risdon W.; Thomson, George H. *AIChE J.* **1979**, *25*, 653.
(9) Carmichael, L. T.; Berry, Virginia M.; Sage, B. H. *J. Chem. Eng. Data* **1969**, *14*, 27.
(10) Merrington, A. C. "Viscometry"; Arnold: London 1949.
(11) Ely, James F.; Hanley, H. J. M. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 323.
(12) Ely, James F., presented at the National Meeting of the American Institute of Chemical Engineers, Houston, TX, March 27–31, 1983.
(13) Shepard, A. F.; Henne, A. L.; Midgley, T., Jr. *J. Am. Chem. Soc.* **1931**, *53*, 1948.

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