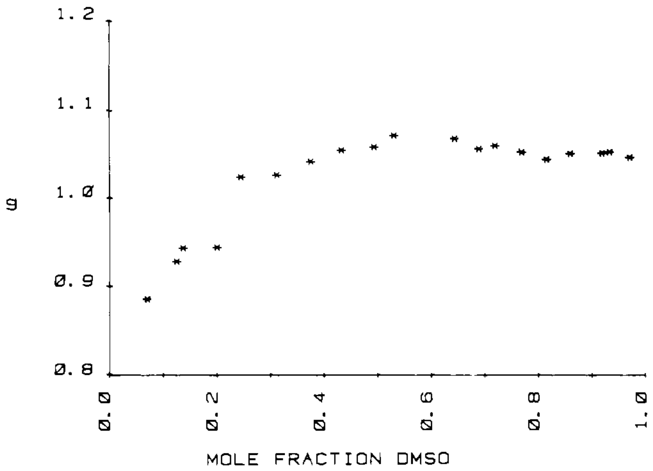

Figure 4. Kirkwood correlation factor vs. mole fraction of Me_2SO.

negative over the entire concentration range.) On the basis of excess molar polarization data, the maximum departure from ideal behavior occurs at about 0.33 mole fraction Me_2SO.

The Kirkwood correlation factors, shown in Figure 4, were evaluated according to eq 8. The gas-phase dipole moment, $\mu_1 = 3.96$ D, was taken from ref *22*. The refractive indices used to approximate the high-frequency permittivity ($\epsilon_\infty \cong 1.1 n_D{}^2$) were $n_1 = 1.45739$ and $n_2 = 1.4773$ (*21*). As in pure Me_2SO, deviations from $g = 1$ are very small, indicating the absence of strong short-range orientational correlations. Nevertheless, in low-concentration solutions g is decidedly less than unity, a result consistent with the negative excess dielectric constants. The values of g for more concentrated solutions are only slightly greater than unity (1.04–1.06 for $x_1 > 0.5$).

Discussion

The limiting value of g as x_1 approaches 1 can be compared to the results of Amey (*10*) and Casteel and Sears (*11*) for pure Me_2SO. Amey calculated a g value slightly less than 1, which was independent of temperature in the range 290–350 K. However, he took $\mu_1 = 4.3$ D, in contrast to $\mu_1 = 3.96$ D used in this work. Our results are more in agreement with those of Casteel and Sears, who found $g = 1.07$ for neat Me_2SO at 298 K, than with those of Amey.

The dielectric data presented here indicate a slight tendency toward antiparallel alignment of neighboring dipoles in dilute solutions of Me_2SO in CCl_4. In view of the evidence from IR spectroscopy (*6*, *7*) that Me_2SO forms dimers in dilute solution in CCl_4, the dielectric data support the interpretation that antiparallel alignment, resulting in net cancellation of dipole moments, is favored in low dielectric constant media. At higher Me_2SO concentrations, on the other hand, g exceeds unity as the dielectric constant increases and aggregates with enhanced net dipole moments are stabilized. Recent evidence based on the observation of simultaneous vibrational transitions of Me_2SO in CCl_4 solution indicates the presence of Me_2SO n-mers over a wide range of concentrations, and theoretical analysis points to the importance of both parallel and antiparallel alignments (*7*). Thus, spectroscopic as well as thermodynamic (*1*–*5*) data support the conclusion that Me_2SO self-associates in nonpolar media, but the dielectric data reveal that the angular dependence of the intermolecular potential is insufficient to favor a particular relative orientation of neighboring dipoles.

Registry No. Me_2SO, 67-68-5; CCl_4, 56-23-5.

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Enthalpies for Toluene and Methylcyclohexane in the Fluid State

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A new electrical-matching, flow calorimeter has been used to measure enthalpies of toluene (333.15–513.15 K, 0.12–9.41 MPa) and of methylcyclohexane (353.15–513.15 K, 0.12–9.41 MPa) in both the liquid and vapor states. Perfect gas state enthalpies and heats of vaporization are shown to be in reasonable agreement with previous experiments and compilations.

Introduction

Liquid-phase heat capacities have been reported from 188.15 to 383.15 K for toluene by Burlew (*1*) and by Timmermans (*2*) plus from 383.15 to 523.15 K by San José et al. (*3*). Vapor-phase heat capacities were reported by Montgomery and DeVries (*4*) from 383.15 to 410.15 K. Yaws (*5*) has reviewed the thermophysical property data for toluene including vapor pressures, heats of vaporization, liquid-phase heat capacities, perfect gas state heat capacities, and saturated-liquid densities from roughly the triple point to critical point tempera-

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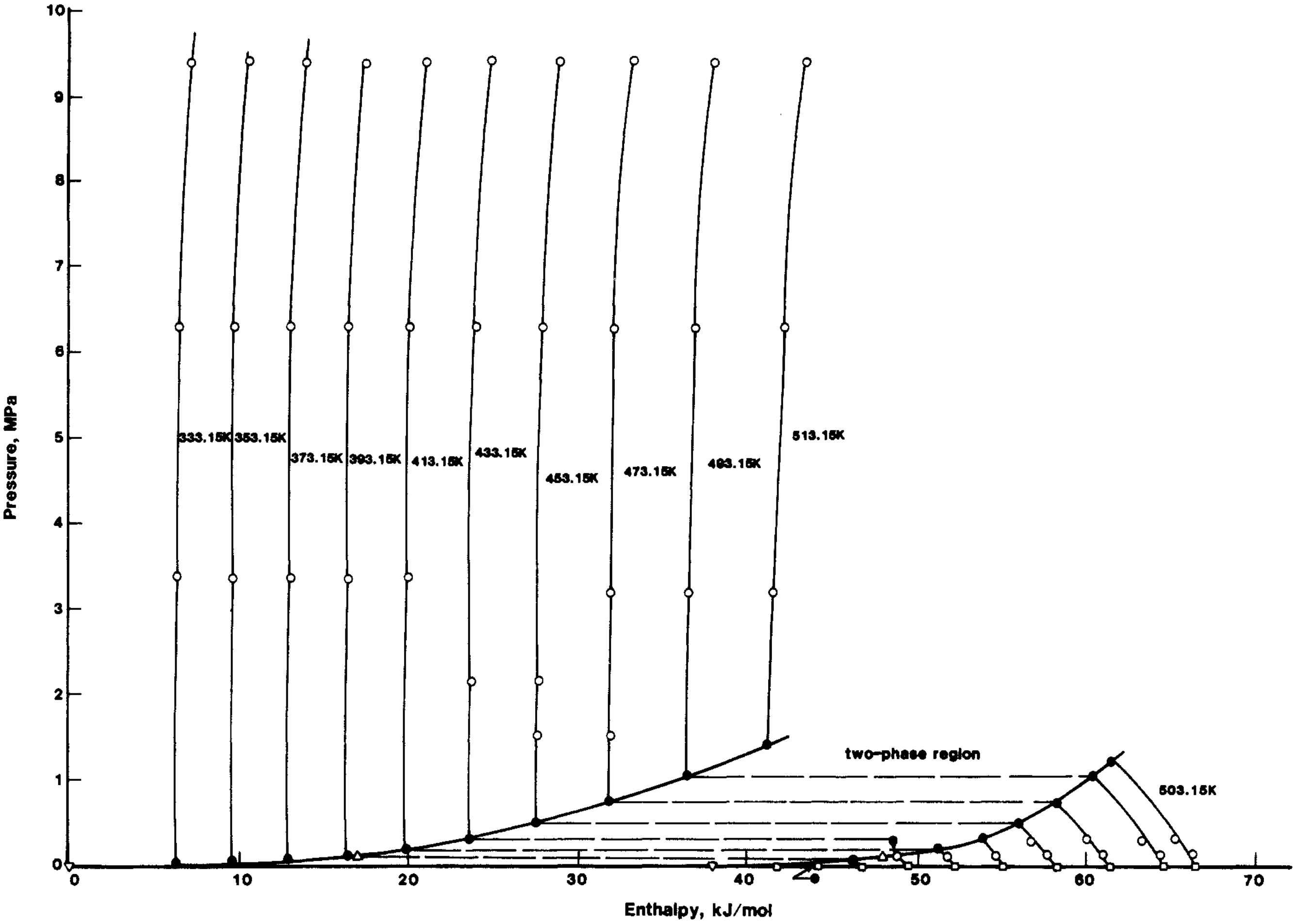

Figure 1. Pressure-enthalpy diagram for toluene ($H = 0$ for saturated liquid at 298.15 K): (○) data points, (□) perfect gas state enthalpies, (▽) saturated liquid and vapor values at 298.15 K from ref *11*, (△) saturated liquid and vapor values at the normal boiling point (383.775 K) from ref *11*, and (●) extrapolated values for saturated liquid and vapor.

ture. Recently, the Thermodynamic Research Center (*6*) has prepared thermophysical tables for toluene.

Existing thermophysical measurements for methylcyclohexane are sparse. Vapor-phase heat capacities were measured in ref *4* from 373.15 to 410.15 K. The TRCHP Tables (*7*) provide vapor pressures and perfect gas state heat capacities.

Experimental Apparatus

Experimental enthalpies, H, for toluene (333.15–513.15 K, 0.12–9.41 MPa) and for methylcyclohexane (353.15–513.15 K, 0.12–9.41 MPa) were measured in both the liquid and vapor states by using a new electrical-matching, flow calorimeter (*8*). Reference *8* contains a complete description of the experimental apparatus, its calibration with water steam, and a detailed analysis of experimental uncertainties. The parts of this analysis pertaining to the toluene and methylcyclohexane data will be repeated here. The dissertation of Cediel (*9*) provides further details for both ref *8* and this manuscript.

The Freon-11, boil-off calorimeter measures the difference between the enthalpy of a fluid or fluid mixture, at some pressure and elevated temperature, and the enthalpy of the same fluid in the liquid state near 25 °C and at the same pressure. During steady-sate operation, Freon is boiled off near 25 °C in the inner calorimeter, the vapor flow rate is measured by a turbine meter, the Freon is condensed then at about 21 °C, and the liquid is returned to the inner calorimeter. This Freon, thermosyphon system is driven by a constant power input to the inner calorimeter. With no experimental fluid flowing through the calorimeter, an electrical-matching heater supplies the total power level as monitored by the turbine meter. Then the hot experimental fluid, which is pumped at a known, constant flow rate, enters the calorimeter supplying a power level that is measured as the difference between the original electrical power input and that now required to maintain the same turbine meter reading. The electrical-matching technique (1) avoids actual measurement of the Freon, boil-off rate, (2) nearly cancels the already small heat leaks, and (3) eliminates the need for an accurate, independent value for the heat of vaporization of Freon-11. Calibration data for water/steam (*8*) show an average difference of 0.2% and maximum differences of 0.7% for enthalpies as compared to modern steam tables.

Chemical Purity

Toluene with a minimum purity of 99.9% was obtained from the Phillips Petroleum Co. Methylcyclohexane of the same minimum purity was obtained from the same supplier. The liquid density at 25 °C was measured to be 0.8669 g/cm^3 for toluene and 0.7694 g/cm^3 for methylcyclohexane (MCH).

Experimental Results

The raw data (*9*) were taken on isobars; the exit liquid from the calorimeter was corrected to our reference state ($H = 0$) of 298.15 K and saturated liquid where the vapor pressure of toluene is 3.793 kPa (28.45 mmHg) and that of MCH is 6.17 kPa (46.3 mmHg). These corrected raw data were then plotted on large graphs of enthalpy vs. temperature for different isobars. Isobaric heat capacities, C_p, the slopes of these graphs, were

Table I. Smoothed Experimental Enthalpy Values for Toluene

T, K	P, MPa	H,[b] kJ/g-mol
	Liquid State	
333.15	3.38	6.35
353.15	3.38	9.63
373.15	3.38	12.95
393.15	3.38	16.36
413.15	3.38	19.90
433.15	2.15	23.61
453.15	2.15	27.51
453.15	1.48	27.47
473.15	1.48	31.84
473.15	3.21	31.91
493.15	3.21	36.50
513.15	3.21	41.49
333.15	6.31	6.37
353.15	6.31	9.67
373.15	6.31	13.02
393.15	6.31	16.45
413.15	6.31	20.01
433.15	6.31	23.76
453.15	6.31	27.77
473.15	6.31	32.10
493.15	6.31	36.84
513.15	6.31	42.09
333.15	9.41	7.23
353.15	9.41	10.55
373.15	9.41	13.92
393.15	9.41	17.37
413.15	9.41	20.99
433.15	9.41	24.81
453.15	9.41	28.88
473.15	9.41	33.28
493.15	9.41	37.95
	Vapor State	
513.15	0.12	43.40
393.15	0.12	48.78
413.15	0.12	51.70
433.15	0.12	54.64
453.15	0.12	57.68
473.15	0.12	60.90
493.15	0.12	64.29
503.15	0.31	66.11
443.15	0.31	55.17
453.15	0.31	56.72
473.15	0.31	59.87
493.15	0.31	63.24
503.15	0.31	65.10

[a] T_c = 591.79 K, P_c = 4.104 MPa, ρ_c = 0.292 g/cm^3. Critical constants from ref *10*. [b] H based upon zero enthalpy for saturated liquid at 298.15 K.

Table II. Smoothed Experimental Enthalpy Values for Methylcyclohexane[a]

T, K	P, MPa	H,[b] kJ/g-mol
	Liquid State	
353.15	0.79	10.99
373.15	0.79	15.16
393.15	0.79	19.60
413.15	0.79	24.37
423.15	0.79	27.11
433.15	2.86	29.37
453.15	2.86	34.51
473.15	2.86	40.10
483.15	2.86	43.37
353.15	3.14	11.53
373.15	3.14	15.58
393.15	3.14	19.87
413.15	3.14	24.46
423.15	3.14	27.25
373.15	6.55	16.28
393.15	6.55	20.53
413.15	6.55	25.05
433.15	6.55	30.01
353.15	7.00	12.24
373.15	7.00	16.40
393.15	7.00	20.65
413.15	7.00	25.10
433.15	7.00	29.80
453.15	7.00	34.83
473.15	7.00	40.22
493.15	7.00	46.07
513.15	7.00	52.51
353.15	9.41	13.04
373.15	9.41	17.17
393.15	9.41	21.40
413.15	9.41	25.76
433.15	9.41	30.33
453.15	9.41	35.19
473.15	9.41	40.47
493.15	9.41	46.25
513.15	9.41	52.62
	Vapor State	
373.15	0.11	46.04
393.15	0.11	49.65
413.15	0.11	53.35
433.15	0.11	57.19
453.15	0.11	61.23
473.15	0.11	65.43
493.15	0.11	69.98
513.15	0.11	75.03
453.15	0.34	60.96
473.15	0.34	65.02
493.15	0.34	69.32
513.15	0.34	73.93
473.15	0.69	64.22
493.15	0.69	68.36
513.15	0.69	72.60

[a] T_c = 572.20 K, P_c = 3.471 MPa, ρ_c = 0.267 g/cm^3. Critical constants from ref *10*. [b] H based upon zero enthalpy for saturated liquid at 298.15 K.

then plotted against temperature on a second series of graphs. Such isobaric curves should be concave upward and monotonically increasing in C_p vs. temperature whether in the liquid or vapor state. Very slight smoothing of these secondary graphs resulted in slight alterations in the original graphs of H vs. T to maintain consistency. Tables I and II contain the final smoothed values for toluene and MCH, respectively. The pressures and temperature found in these tables match closely the raw data points—in effect only the enthalpy values have been adjusted slightly by the smoothing process. The magnitudes of these adjustments were always within the experimental uncertainties discussed below.

Entropies based upon the same reference state were calculated along isobars from the enthalpies of Tables I and II. The tabulated values plus entropy vs. temperature diagrams are given in ref *9*.

Experimental Uncertainties

An error analysis together with calibration data for water/steam (*8*) shows the maximum total uncertainty in the present enthalpies to be 0.40% at 373.15 K increasing to 0.50% at 573.15 K. Using linear interpolation or extrapolation at the lower temperatures, the reader may estimate the uncertainty at any temperature of Tables I and II. Examples are (1) toluene liquid at 513.15 K and 9.41 MPa where H = 43.40 ± 0.20 kJ/g-mol, (2) toluene vapor at 503.15 K and 0.31 MPa where H = 65.10 ± 0.30 kJ/g-mol, (3) MCH liquid at 353.15 K and 0.79 MPa where H = 10.99 ± 0.04 kJ/g-mol, (4) MCH vapor at 373.15 K and 0.11 MPa where H = 46.04 ± 0.18 kJ/g-mol, and (5) MCH vapor at 513.15 K and 0.69 MPa where H = 72.60 ± 0.34 kJ/g-mol.

Discussion of Results

Figures 1 and 2 are the pressure/enthalpy diagrams for toluene and methylcyclohexane, respectively. The present

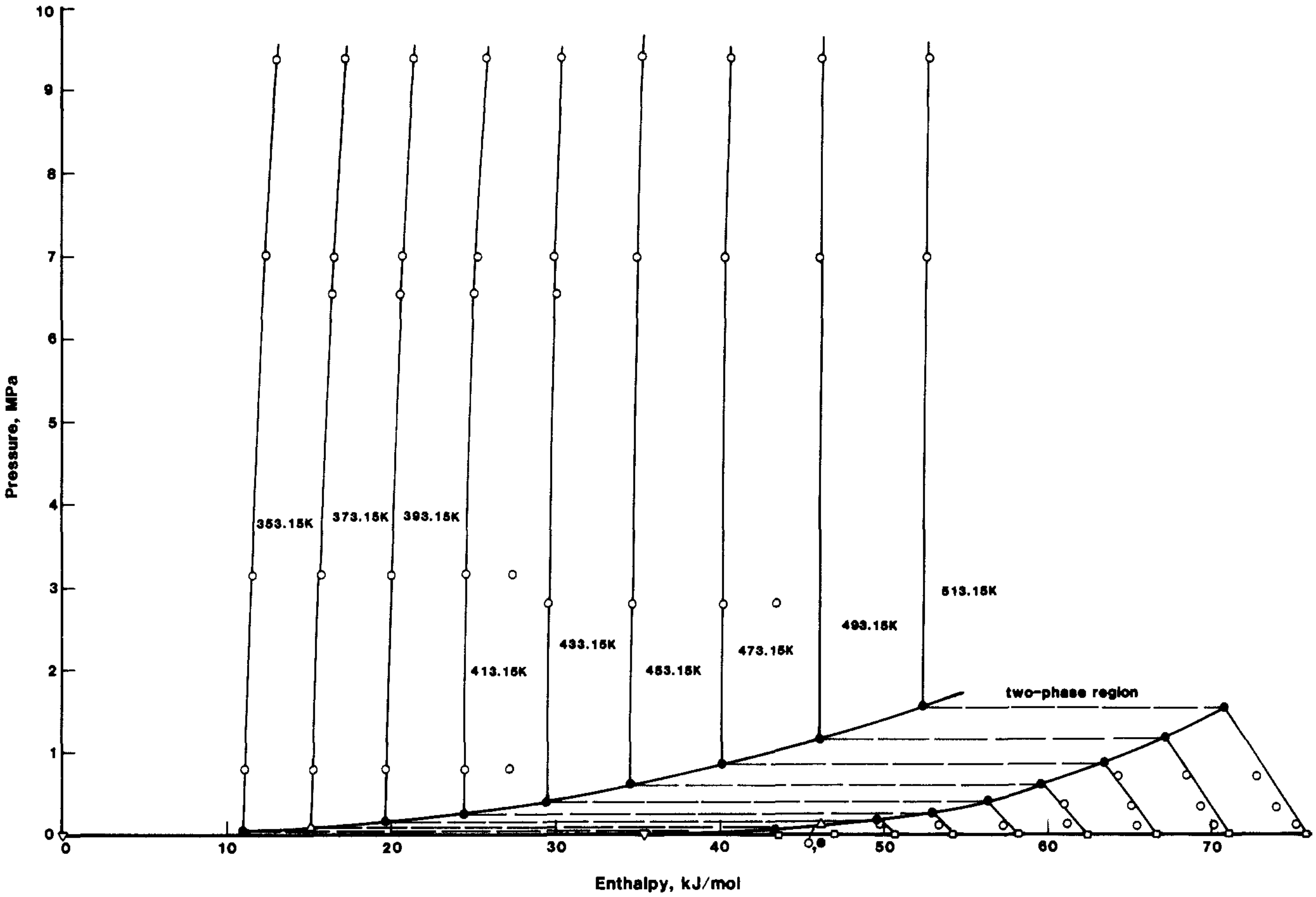

Figure 2. Pressure-enthalpy diagram for methylcyclohexane ($H = 0$ for saturated liquid at 298.15 K). See Figure 1 for legend.

Table III. Perfect Gas State Enthalpies

T, K	H^*,[a] kJ/g-mol toluene	methylcyclohexane
333.15	41.77	
353.15	44.17	43.55
373.15	46.72	46.91
393.15	49.41	50.47
413.15	52.21	54.22
423.15		56.16
433.15	55.13	58.15
453.15	58.18	62.28
473.15	61.35	66.57
493.15	64.61	71.05
503.15	66.28	
513.15	67.97	75.69

[a] H^* based upon zero enthalpy for saturated liquid at 298.15 K.

vapor measurements are seen to be in close alignment with the perfect gas state values of ref *7*, which are given in Table III.

Heats of vaporization can be approximated by extrapolation of the liquid and vapor isotherms to the vapor pressure. The latter were estimated from the Antoine constants of Zwolinski and Wilhoit (*11*). This reference further provides the heat of vaporization of toluene as 37.99 kJ/g-mol at 298.15 K and 33.18 kJ/g-mol at 383.775 K (NBP); the corresponding values for MCH are 35.36 kJ/g-mol at 298.15 K and 31.13 kJ/g-mol at 374.084 K (NBP). Table IV shows our estimated heats of vaporization from Figures 1 and 2 to agree with those of ref *11* to within our experimental uncertainty. Table V provides liquid-state heat capacities for toluene by differentiation of our enthalpy data. Our heat capacities, which should be accurate to ±2%, agree well with those of ref *3* at the higher temperatures of Table V but the disagreement is about 6% at 353.15 K. The values of ref 3 increase less with temperature than here.

Table IV. Heats of Vaporization (λ)

	toluene		methylcyclohexane	
T, K	P^σ, MPa	λ, kJ/g-mol	P^σ, MPa	λ, kJ/g-mol
333.15	0.0185	35.4		
353.15	0.0388	34.4	0.0539	32.3
373.15	0.0742	33.4	0.0987	31.1
393.15	0.1313	32.4	0.1682	29.9
413.15	0.2181	31.4	0.2704	28.5
433.15	0.3434	30.2	0.4135	26.9
453.15	0.5166	28.4	0.6061	25.2
473.15	0.7476	26.4	0.8568	23.4
493.15	1.0461	24.0	1.1738	21.1

Table V. Heat Capacity of Liquid Toluene at 2 MPa

	C_p, kJ/(g-mol K)	
T, K	ref *3*	this work
353.15		0.166
373.15		0.170
393.15	0.189	0.175
413.15	0.195	0.182
433.15	0.203	0.192
453.15	0.212	0.206
473.15	0.221	0.222
493.15	0.233	0.240

Registry No. Toluene, 108-88-3; methylcyclohexane, 108-87-2.

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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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