of decanol), and the curves are rather wide ($A_1 \sim 2$).

It is interesting to compare the critical temperatures of polar liquid–aliphatic alcohol and polar liquid–aliphatic hydrocarbon systems. The differences in critical-temperature decrease induced by the OH group are basically due to the formation of hydrogen bonds between components. The data necessary for estimation are not available for decane, but ref *4* gives the appropriate values for heptane. The critical-temperature changes after replacing heptane with decanol are -65, -61, -57, -41, and -14 K for dimethyl phthalate, acetonitrile, phenylacetonitrile, 1,2-ethylene diacetate, and nitroethane, respectively. The results are in agreement with the fact that the NO_2 group shows a weak ability to form hydrogen bonds.

The electric permittivity of the investigated liquids ranged from 7 to 35. Two of the systems have well-matched electric permittivities; for ethylene diacetate and dimethyl phthalate the difference $\Delta\epsilon$ at 298.16 K is ~0.60. Decanol also forms a critical system with *o*-nitroanisole ($\epsilon \sim 45$); however, the critical temperature is higher than 300 K.

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The advice and interest of Professor A. Piekara in the present work is greatly appreciated. One of the authors (W.P.) is also indebted to Dr. T. Krupkowski for critical discussion.

Glossary

A_1, A_2, a_1,a_2	constants of the coexistence-curve equations
T	absolute temperature, K
T_c	critical temperature
t	reduced temperature
X_c	critical concentration
$X_\pm$	equilibrium concentrations of coexisting liquids

Greek Letters

α	critical exponent for specific heat
β	critical exponent for coexistence curve
Δ	correction exponent in eq 1
ϵ	electric permittivity
$\Delta\epsilon$	electric permittivity difference between decanol and a dipolar liquid
ϕ	concentration in volume fraction
ϕ_c	critical concentration in volume fraction

Subscripts

c	critical

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Vapor–Liquid Phase Equilibrium for Carbon Dioxide–*n*-Hexane at 40, 80, and 120 °C

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Vapor and liquid equilibrium phase compositions have been measured for carbon dioxide–*n*-hexane at temperatures of 40, 80, and 120 °C. At each temperature, the pressure range from ~6.8 atm (100 psia) to near the system critical pressure was covered. Equilibrium *K* values for carbon dioxide and *n*-hexane were calculated from these data. The data from this work are well represented by the Soave equation of state. When one uses an optimum interaction parameter, C_{12} = 0.131, in the Soave equation, average errors in the predicted phase compositions (at fixed T and P) are 0.012 and 0.009 for the liquid and vapor phases, respectively.

Introduction

Carbon dioxide–hydrocarbon mixtures are found in numerous processes of importance to the production of fluids for use as energy sources. Prime process examples include the carbon dioxide flooding of petroleum reservoirs and the conversion of coal to liquid fuels. Furthermore, prediction of the behavior of mixtures which contain carbon dioxide is known to require modification of the simple mixing rules employed in commonly used solution models. To evaluate the parameters required to characterize carbon dioxide–hydrocarbon interactions requires experimental data on such systems. Systematic studies of selected carbon dioxide–hydrocarbon systems are especially valuable since such data can form the basis for generalizations of the interaction parameters in carbon dioxide systems.

Our recent study of the literature on phase equilibrium for carbon dioxide–*n*-paraffin hydrocarbons raised questions regarding the accuracy of the available data for carbon dioxide–*n*-hexane. As a result, the present study was undertaken to provide additional information on this binary system.

Experimental Method

The experimental measurements were done in a variable-volume, windowed, phase equilibrium cell. The cell is constructed of A286 stainless steel and has a maximum volume of 600 cm^3. The cell is basically a 2.0-in. i.d., 4.5-in. o.d. piston–cylinder assembly, with the cylinder closed at one end by a metal plug. The opposite end contains a 2.75-in. diameter, 1.0-in. thick quartz window, backed by a metal plug except for

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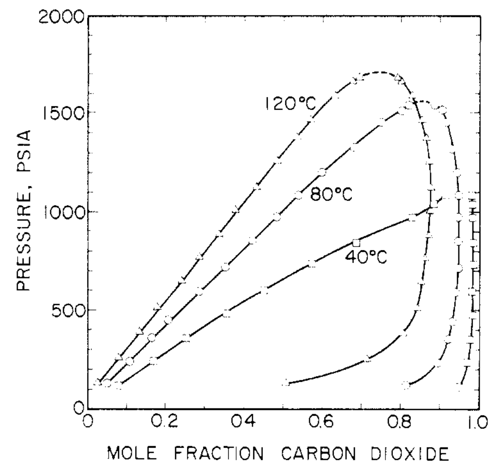

Figure 1. Isothermal pressure-composition data for carbon dioxide–*n*-hexane.

a 2.125 × 0.15 in. slit through which the cell contents may be viewed. A floating piston, fitted with a "Kalrez" O-ring at each end, was used to confine the mixture under study. The volume on the backside of the piston contained silicon oil which was used as a driving fluid to position the piston and, thereby, regulate the system pressure.

The cell was mounted in a rocking air bath which could be rocked at variable speeds and angles of rotation up to a maximum of 10 cycles/min and 120° total angle. This rocking action was employed to hasten equilibration of the phases in the cell. The bath itself contained two U-shaped ducts through which air was circulated by blowers mounted at opposite ends of the bath. Rod-type heaters inside the ducts supplied the necessary energy to maintain the desired bath temperature. Temperatures were measured by a calibrated platinum resistance thermometer imbedded in the cell body. Temperatures are estimated to be accurate to ±0.05 °C; temperature fluctuations in the cell were of this same magnitude. The system pressure was monitored by a transducer mounted in the cell wall, and final pressure readings were made on a calibrated bourdon-type pressure gauge. Reported pressures are estimated to be accurate to ±2 psia.

Vapor and liquid samples were taken in sample valves of the type described by Yarborough and Vogel (*1*) and were analyzed on a Varian Model 3700 chromatograph with a thermal conductivity detector. The sample valves were heated to 105 °C before sample injection. A column reversal technique was employed in the analyses using columns of Porapak N (4 ft) and 5% OV101 on Chromosorb G (6 ft). The first column was maintained at 110 °C and the second was held at 60 °C until the CO_2 eluted; then the temperature was raised to 120 °C. A constant relative response factor (CO_2/C_6) of 1.579 was used in the analyses, based on calibrations employing mixtures of known composition prepared in the equilibrium cell. Each reported phase composition represents the average value from analyses of from two to eight replicate samples. The average absolute percent deviations from the average values ranged from 0.4 to 3.3%.

Materials

The carbon dioxide used in the studies was 99.99 mol % purity, supplied by Linde, and the *n*-hexane was 99.0 mol % minimum purity from Phillips Petroleum Co. Both were used without further purification.

Results

The experimental data are presented in Table I and Figures 1 and 2. (Solid lines in the figures are drawn by inspection.)

Table I. Carbon Dioxide-*n*-Hexane Vapor-Liquid Equilibrium Data

press., psia	mole fraction CO_2 liquid	mole fraction CO_2 vapor	*K* values CO_2	*K* values n-C_6H_{14}
		40 °C		
113	0.080	0.949	11.85	0.055
240	0.170	0.972	5.73	0.034
354	0.252	0.977	3.87	0.031
480	0.356	0.982	2.76	0.027
600	0.450	0.982	2.18	0.032
733	0.574	0.984	1.71	0.037
844	0.687	0.985	1.44	0.048
973	0.829	0.984	1.19	0.091
1039	0.882	0.982	1.11	0.149
1085	0.915	0.981	1.07	0.221
		80 °C		
125	0.052	0.815	15.83	0.195
237	0.110	0.894	8.15	0.119
355	0.167	0.923	5.52	0.092
444	0.207	0.934	4.50	0.084
593	0.287	0.943	3.29	0.080
719	0.353	0.948	2.69	0.080
854	0.422	0.947	2.24	0.092
973	0.486	0.947	1.95	0.102
1084	0.541	0.949	1.75	0.112
1203	0.599	0.945	1.58	0.137
1327	0.683	0.930	1.36	0.220
1458	0.752	0.918	1.22	0.330
1518	0.805	0.906	1.13	0.480
1546	0.821	0.886	1.08	0.639
		120 °C		
130	0.028	0.507	17.83	0.508
251	0.080	0.715	8.93	0.310
383	0.135	0.808	5.98	0.223
511	0.180	0.843	4.67	0.191
644	0.243	0.853	3.51	0.194
769	0.289	0.862	2.99	0.194
885	0.339	0.873	2.58	0.193
1008	0.380	0.875	2.30	0.202
1125	0.433	0.877	2.03	0.216
1259	0.486	0.874	1.80	0.245
1379	0.538	0.866	1.61	0.290
1464	0.570	0.853	1.50	0.341
1593	0.632	0.828	1.31	0.467
1661	0.676	0.801	1.19	0.615
1682	0.693	0.793	1.15	0.675

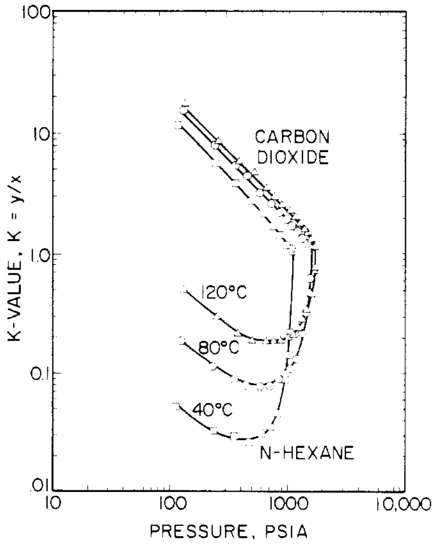

Figure 2. Vaporization equilibrium ratios (*K* values) for carbon dioxide–*n*-hexane.

These results are substantially different from the work of Ohgaki and Katayama (*2*); Figure 3 compares the two data sets at 40 °C. In general, the liquid-phase compositions from the previous

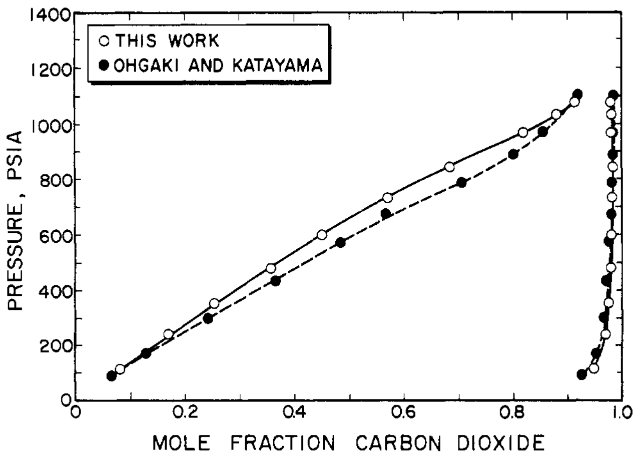

Figure 3. Comparison of pressure-composition data at 40 °C for carbon dioxide–*n*-hexane.

study are lower in *n*-hexane than those of the present study. At 500 psia, this difference is 6 mol %, and the difference in the *K* values for *n*-hexane is ~25%.

Correlation

The data from the present work have been correlated by the Soave equation of state (*3*), with the mixing rules

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij}$$

$$b = \sum_{i=1}^{N} y_i b_i$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - C_{ij})$$

where C_{ij} is an empirical interaction parameter. In this work, the value C_{ij} was determined by minimizing the sum of squares, SS, of errors in the predicted phase compositions at fixed temperature and pressure

$$SS = \sum_{i=1}^{M} \{(\Delta x)^2 + (\Delta y)^2\}_i$$

Table II. Soave Correlation of Carbon Dioxide–*n*-Hexane Data

temp, °C	optimum C_{ij}	rms error in mole fraction	
		liquid	vapor
	Present Work		
40	0.125	0.011	0.002
80	0.130	0.009	0.004
120	0.139	0.006	0.013
all	0.131	0.012	0.009
	Oghaki and Katayama		
40	0.090	0.018	0.006

Table II presents values of C_{ij} evaluated from the data of the present work at each separate isotherm and from all of the data treated simultaneously. Also shown is the result of similar treatment of the data of Ohgaki and Katayama at 40 °C. As shown in Table II, when all data from the present work are treated simultaneously, root-mean-square (rms) errors of 0.012 and 0.009 result in the liquid- and vapor-phase mole fractions, respectively.

Careful analysis of the data from the present work reveals increased scatter in the data near the critical point. The data were reanalyzed by deleting data points at the two highest pressures on each isotherm; the optimum C_{ij} was unaffected (0.131), but errors in the predicted vapor mole fraction were reduced by a factor of 2 (to 0.005) while the liquid-phase prediction was unaffected. In this case, average absolute errors in the predicted *K* values are 5% for CO_2 and 6% for *n*-hexane. When all data are included, the errors are 4 and 13%, respectively.

Glossary

a, *b*	parameters in Soave equation of state
C_{ij}	empirical interaction parameter in Soave equation
M	total number of data points
N	total number of components in mixture
x	mole fraction CO_2 in liquid phase
y	mole fraction CO_2 in vapor phase
Δ	difference between experimental and calculated value

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Excess Gibbs Energy for Eight Oleic Acid–Solvent and Triolein–Solvent Mixtures at 318.15 K

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Vapor pressures of eight oleic acid–solvent and triolein–solvent mixtures have been determined on a static apparatus at 318.15 K. Activity coefficients and excess Gibbs energies have been derived from the data. The solvents with oleic acid are methanol, ethanol, 2-propanol, acetone, and *n*-hexane, while the solvents with triolein are 2-propanol, acetone, and *n*-hexane.

Introduction

The C_{17} and C_{18} fatty acids and their glycerides are of considerable importance in the soap and food industries. The separation of these high-molecular-weight compounds is generally effected by energy-intensive processes such as fractional crystallization. Alternative methods of separation are liquid extraction and extractive distillation. We therefore examine the excess thermodynamic properties of some fatty acid–solvent and glyceride–solvent systems, to help assess the suitability of these methods.

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