σ standard deviation

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Vapor-Liquid Equilibrium in Binary Mixtures of Carbon Dioxide + Diphenylmethane and Carbon Dioxide + 1-Methylnaphthalene

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Vapor-liquid equilibrium data for binary mixtures of carbon dioxide with diphenylmethane and with 1-methylnaphthalene are determined at temperatures between 189 and 430 °C and at pressures between 20 and 50 atm.

Introduction

Carbon dioxide is an important nonhydrocarbon component in petroleum reservoir fluids and natural gases and is encountered in coal conversion processes. Phase equilibrium data on carbon dioxide mixtures are, therefore, of considerable industrial and engineering interest. We (*5*) recently reported vapor-liquid equilibrium data in binary mixtures of carbon dioxide + *n*-decane and carbon dioxide + *n*-hexadecane and reviewed the literature on carbon dioxide + heavy paraffins. In this work we report the compositions of saturated equilibrium liquid and vapor phases for binary mixtures of carbon dioxide + diphenylmethane and carbon dioxide + 1-methylnaphthalene at temperatures between 189 and 430 °C and at pressures between 20 and 50 atm.

No phase equilibrium data have been previously reported for these two binary systems at the temperature and pressures of this work. Tremper and Prausnitz (*9*) measured low-pressure solubilities up to 200 °C. A few other studies have been reported on mixtures of CO_2 with aromatic hydrocarbons but all were limited to temperatures below those of this work. Ng and Robinson (*3*) reported data for carbon dioxide + toluene mixtures at 38-204 °C and at pressures up to 151 atm. Ohgaki and Katayama (*4*) and Wan and Dodge (*10*) determined solubility of CO_2 in benzene at temperatures up to 60 °C. Luks and Kohn and co-workers (*2*, *8*, *11*) studied binary mixtures of carbon dioxide + 2-methylnaphthalene and carbon dioxide + butylbenzene at low temperatures and ternary mixtures of carbon dioxide + *n*-decane + 2-methylnaphthalene and carbon dioxide + butylbenzene + 2-methylnaphthalene. Francis (*1*) measured solubilities of CO_2 in aromatic compounds at 25 °C.

Table I. Carbon Dioxide + Diphenylmethane Vapor-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_D
		189.6 °C		
18.90	0.0572	0.9886	17.28	0.0121
19.84	0.0594	0.9892	16.65	0.0115
29.69	0.0876	0.9921	11.33	0.00866
40.1	0.1163	0.9933	8.541	0.00758
49.6	0.1429	0.9938	6.955	0.00723
		269.4 °C		
20.17	0.0512	0.9329	18.22	0.0707
30.01	0.0777	0.9505	12.23	0.0537
39.8	0.1017	0.9582	9.422	0.0465
50.3	0.1283	0.9634	7.509	0.0420
		350.2 °C		
19.17	0.0394	0.7127	18.09	0.2991
30.67	0.0684	0.7999	11.69	0.2148
40.0	0.0925	0.8338	9.014	0.1831
49.4	0.1155	0.8567	7.417	0.1621
		430.6 °C		
29.45	0.0505	0.4303	8.521	0.6000
40.2	0.0818	0.5312	6.494	0.5106
50.0	0.1127	0.5915	5.249	0.4604

Experimental Section

The apparatus and procedure used in this study have been described previously by Simnick et al. (*6*). A minor change has been made in the apparatus with the addition of a Heise gauge (Model CMM) which measures pressures below 34 atm to an increased accuracy of ±0.03 atm.

The apparatus is of the flow type to minimize thermal decomposition of the hydrocarbons at high temperatures. The

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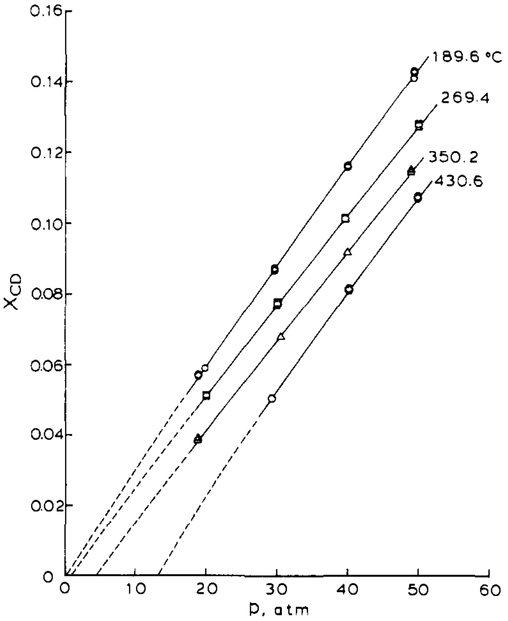

Figure 1. Solubility of CO_2 in diphenylmethane.

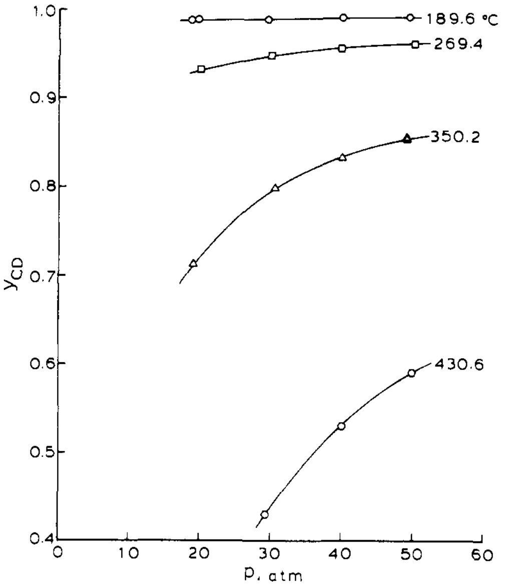

Figure 2. Mole fraction of CO_2 in saturated vapor in carbon dioxide + diphenylmethane.

attainment of equilibrium in the apparatus has been checked by careful studies described in previous reports from this laboratory (*6*, *7*, *12*).

Carbon dioxide was supplied by Matheson with a minimum purity of 99.99% (Coleman Instrument grade). Hydrocarbon solvents were purchased from Aldrich Chemical Co. with a reported purity of 99% for diphenylmethane and 97% for 1-methylnaphthalene. These compounds were further purified by fractional distillation under a reduced nitrogen pressure before use. The purities of the chemicals after distillation were found to be higher than 99% by gas chromatography analysis. Samples of the condensate from the cell effluents of both gas and liquid streams of all the runs were analyzed by gas chromatography. No impurity due to thermal decomposition was noticed.

Results

The experimental vapor-liquid equilibrium data for the binary system carbon dioxide + diphenylmethane are reported in Table I at four temperatures from 189.9 to 430.4 °C. The pressures are from 20 to 50 atm for each temperature. The equilibrium compositions in the table are the averages of at least two data points for both x and y samples. The reproducibility of the duplicate samples is generally within 1%. Figures 1 and 2 show the isothermal compositions for liquid and vapor phases, respectively, as a function of total pressure. The individual samples are shown in the figures as separate points when they can be distinguished. Figure 1 also shows the extrapolation of the isothermal composition curve to join the vapor pressure of diphenylmethane at $x_{CD} = 0$. The vapor pressure data were taken from Simnick et al. (*7*).

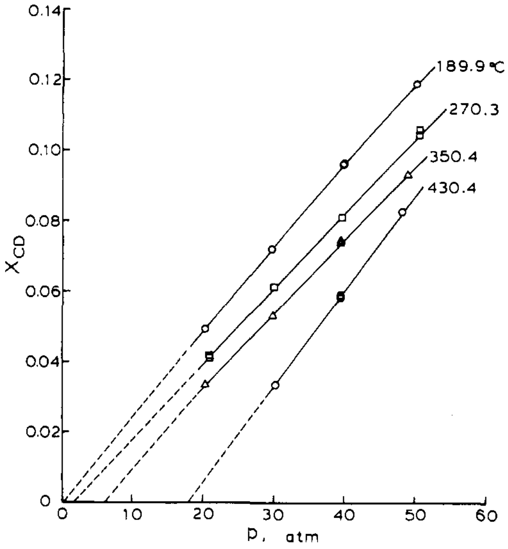

Figure 3. Solubility of CO_2 in 1-methylnaphthalene.

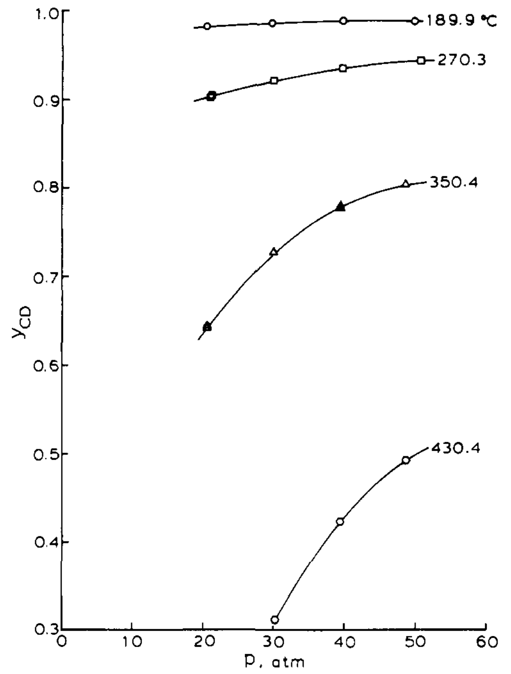

Figure 4. Mole fraction of CO_2 in saturated vapor in carbon dioxide + 1-methylnaphthalene.

Table II presents the experimental results for the carbon dioxide + 1-methylnaphthalene system. The equilibrium compositions are shown in Figure 3 for liquid phase and Figure 4 for vapor phase. The vapor pressures indicated in Figure 3 were taken from Yao and co-workers (*12*). The solubility of CO_2 in 1-methylnaphthalene has been found to be significantly lower than in diphenylmethane at all conditions of this study.

Table II. Carbon Dioxide + 1-Methylnaphthalene Vapor-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_M
		189.9 °C		
20.47	0.0499	0.9836	19.71	0.0173
29.73	0.0730	0.9877	13.53	0.0133
39.9	0.0967	0.9898	10.24	0.0113
50.2	0.1198	0.9903	8.266	0.0110
		270.3 °C		
20.95	0.0422	0.9024	21.38	0.1019
30.04	0.0622	0.9239	14.85	0.0811
39.8	0.0821	0.9376	11.42	0.0680
50.8	0.1061	0.9461	8.917	0.0603
		350.4 °C		
20.56	0.0336	0.6423	19.12	0.3701
30.03	0.0533	0.7288	13.67	0.2865
39.6	0.0745	0.7790	10.46	0.2388
48.9	0.0942	0.8065	8.562	0.2136
		430.4 °C		
30.19	0.0338	0.3112	9.207	0.7129
39.4	0.0584	0.4236	7.253	0.6121
48.3	0.0831	0.4936	5.940	0.5523

Glossary

K	vaporization equilibrium ratio, $K = y/x$
p	pressure, atm
t	temperature, °C
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Subscript

CD	carbon dioxide
D	diphenylmethane
M	1-methylnaphthalene

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Vapor–Liquid Phase Equilibria in the Ternary System Hydrogen + Methane + Tetralin

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Vapor–liquid phase equilibrium of ternary mixtures of H_2 + CH_4 + tetralin was studied at two temperatures, 462 and 663 K, and at pressures from 50 to 250 atm. Relative concentrations of hydrogen to methane were varied, and three observations were made at each condition of temperature and pressure. The response of the *K* values to changing compositions was determined.

Introduction

This work is part of a continuing study of phase equilibrium in mixtures of light gases and heavy liquids at elevated temperatures and pressures. Reports from this laboratory have so far been almost exclusively concerned with binary mixtures of one light gas plus one heavy liquid, the only exceptions being two ternary mixtures of hydrogen in mixed solvents (*5*). In this work we report ternary mixtures of two light gases plus one solvent. The relative concentrations of hydrogen to methane were systematically varied, and three observations were made at each temperature and pressure in order to reveal the response of the *K* values to the changing compositions.

No phase equilibria data on this ternary system have appeared in the literature, but the constituent binaries hydrogen + tetralin (*8*) and methane + tetralin (*7*) have been reported. Previous studies of ternary mixtures of hydrogen and methane were all related to light solvents at much lower temperatures (*1–4*, *6*).

Experimental Section

The apparatus used in this study was for the most part the same as described by Simnick et al. (*8*). However, changes were made in the gas feed system and in the sampling and analysis systems.

A Matheson gas mixer (Dyna-Blender Model SP-1601) has been installed to provide a mixed gas stream at a set composition from individual cylinders of hydrogen and methane. Composition of the mixed gas was found to stay constant within ±0.5 mol %.

Downstream from the blender two vessels of about 1 L each were placed in series in front of the compressor in order to reduce pressure fluctuations and to promote mixing.

Effluents from the equilibrium cell were reduced in pressure and cooled in the same way as previously described (*8*) to produce a liquid stream and a gas stream. The quantity of the gas stream was measured volumetrically and the liquid gravimetrically. For determination of the gas composition, the separated gas streams were sampled in a sample valve, and the samples were picked up by a stream of helium gas. A Carle 111-H gas chromatograph received the helium-carried stream

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