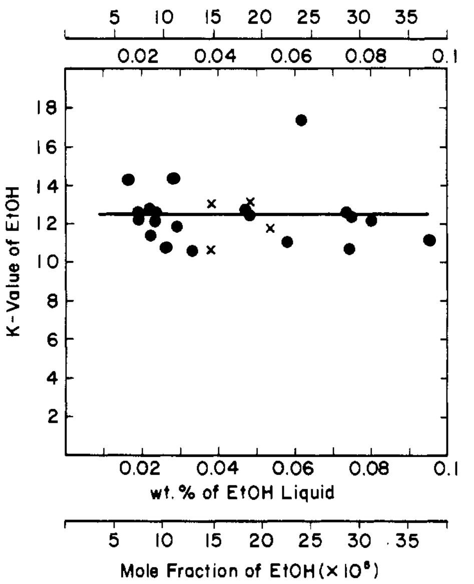

Figure 3. *K* value vs. mole fraction of EtOH: (●) this work; (×) Dalager (4); (—) averaged *K* value with data of this work (12.4).

to a temperature of ~5 °C less than the boiling point of the solution. Ca. 30 min was required for the liquid volumes within the condensate collector and disengagement vessel to reach steady state. The liquid volumes in each of these portions of the apparatus were ca. 10 and 30 mL, respectively. It was determined that a period of 2-3 h was required for true equilibrium to be attained. After this start-up period, 1-mL samples were withdrawn from the disengagement vessel and the condensate collector and analyzed for ethanol and water concentrations.

Results and Discussion

To assure that equilibrium was attained in our apparatus, we took eight equilibrium data points at different concentrations above 4 wt % ethanol and compared them with the previously reported data. As shown in Figure 2, our data agree satisfactorily with those in earlier reports. The entrainment of the liquid droplets in the vapor phase from the disengagement vessel was checked by introducing a nonvolatile component, glucose, to the reservoir and then checking for glucose in the condensate collector with a glucose analyzer (Beckman, No. 92634, Fullerton, CA). Glucose was not detected in the condensate.

Thirty equilibrium data points in the concentration range of 0.01~1.0 wt % were obtained. These are listed in Table I and shown in Figure 2. The temperature inside the disengagement vessel fluctuated in the range of 99.4 ± 0.4 °C. The calculated *K* values and the activity coefficients for ethanol (pure vapor pressure of 1635 mmHg (*4*) at 99.4 °C) and water (pure vapor pressure of 760 mmHg) are also listed in Table I. The calculated *K* values including 20 data points in the concentration range of 0.01-0.1 wt % are plotted in Figure 3. They compared well with Dalager's results, $K = 13.4 \pm 0.5$ (*4*). By assuming the *K* value to be a constant at dilute concentrations, we can calculate the average *K* value of the 20 experimental results taken at concentrations of 0.01~0.1 wt % to be 12.4 with a standard deviation of 1.5.

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Vapor–Liquid Equilibrium of the Hydrogen + Carbon Dioxide + Quinoline System at Elevated Temperatures and Pressures

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Vapor–liquid equilibrium in ternary mixtures of hydrogen, carbon dioxide, and quinoline was measured at two temperatures, 543 and 703 K, over a pressure range from 50 to 250 atm. Relative concentrations of hydrogen to carbon dioxide were varied, and three observations were made at each condition of temperature and pressure. The variation of gas composition has a significant effect on the *K* values of quinoline at higher pressures.

Introduction

The increasing interest of recent years in processing of coal and other nonpetroleum fossil fuels has resulted in a need for phase equilibrium data at high temperatures and pressures. As part of a continuing study of phase equilibrium in mixtures of light gases and heavy liquids, we report in this work experimental results of vapor–liquid equilibrium phase compositions for ternary mixtures of hydrogen + carbon dioxide + quinoline.

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Table I. Hydrogen + Carbon Dioxide + Quinoline Vapor-Liquid Equilibrium Data

T, K	p, atm	x_H	x_{CD}	x_Q	y_H	y_{CD}	y_Q
					0.7585[a]	0.2415[a]	
543.2	50.1	0.02014	0.01965	0.96021	0.7407	0.2129	0.0464
543.2	100.7	0.0401	0.0406	0.9193	0.7435	0.2290	0.0275
543.1	150.9	0.0591	0.0579	0.8830	0.7468	0.2312	0.0220
543.2	200.0	0.0785	0.0753	0.8462	0.7474	0.2335	0.0191
543.4	248.7	0.0961	0.0889	0.8150	0.7502	0.2321	0.0177
					0.8439[a]	0.1561[a]	
543.3	49.7	0.02184	0.01214	0.96602	0.8280	0.1260	0.0460
543.3	101.2	0.0439	0.0245	0.9316	0.8349	0.1378	0.0273
543.4	151.0	0.0652	0.0374	0.8974	0.8375	0.1418	0.0207
543.3	200.8	0.0851	0.0495	0.8654	0.8379	0.1449	0.0172
543.3	250.0	0.1027	0.0592	0.8381	0.8381	0.1460	0.0159
					0.9186[a]	0.0814[a]	
543.1	49.7	0.0230	0.00698	0.97002	0.8856	0.0689	0.0455
543.2	98.6	0.04641	0.01260	0.94099	0.9045	0.0689	0.0266
543.1	153.1	0.06960	0.01981	0.91059	0.9113	0.0700	0.0187
543.1	200.8	0.0898	0.0245	0.8857	0.9140	0.0707	0.0153
543.1	248.5	0.1085	0.0290	0.8625	0.9149	0.0716	0.0135
					0.7496[a]	0.2504[a]	
703.5	50.0	0.02482	0.01558	0.95960	0.3706	0.1286	0.5008
703.3	101.1	0.0646	0.0380	0.8974	0.5291	0.1727	0.2982
703.5	152.2	0.1015	0.0603	0.8382	0.5695	0.1978	0.2327
703.5	199.0	0.1303	0.0844	0.7853	0.5799	0.2253	0.1948
703.3	251.6	0.1673	0.1097	0.7230	0.5952	0.2303	0.1745
					0.8327[a]	0.1673[a]	
703.4	50.5	0.02816	0.01054	0.96130	0.4195	0.0825	0.4980
703.3	100.0	0.0695	0.0266	0.9039	0.5892	0.1163	0.2945
703.4	149.8	0.1115	0.0381	0.8504	0.6536	0.1251	0.2213
703.3	200.0	0.1492	0.0534	0.7974	0.6736	0.1398	0.1866
703.3	250.8	0.1853	0.0652	0.7495	0.6939	0.1432	0.1629
					0.9184[a]	0.0816[a]	
703.5	50.2	0.03058	0.00505	0.96437	0.4640	0.0400	0.4960
703.3	99.7	0.07704	0.01214	0.91082	0.6558	0.0539	0.2903
703.4	150.1	0.12024	0.01957	0.86019	0.7207	0.0635	0.2158
703.5	201.2	0.1598	0.0248	0.8154	0.7604	0.0637	0.1759
703.5	249.1	0.1952	0.0297	0.7751	0.7787	0.0666	0.1547

[a] Feed gas.

No data on this ternary system have been reported in the literature, although data on the constituent binaries, hydrogen + quinoline (*1*) and carbon dioxide + quinoline (*2*) are available.

Experimental Section

The experimental apparatus and procedure used in this work were basically the same as those described in detail by Simnick et al. (*3*). The apparatus is of the flow type and has been used in several studies of binary mixtures. However, modifications were made in the gas feed system and in the method of sample analysis. A description of the changes was recently given by Simnick and co-workers (*4*).

Measurements were made at two temperatures, 543 and 703 K, and at five pressures from 50 to 250 atm. At each condition of temperature and pressure, equilibrium compositions were determined at three relative concentrations of hydrogen to carbon dioxide. The changes in equilibrium composition were obtained by using three different binary gas feed compositions at ca. 75, 84, and 92 mol % hydrogen. The response of the *K* values to the changing phase compositions was studied.

Hydrogen gas was supplied by Airco with a reported minimum purity of 99.95%. Carbon dioxide was obtained from Matheson with a purity of 99.99%. Quinoline purchased from Fisher Scientific Co. was certified reagent grade of 99+% purity, but showed a deep purple color. The color was removed by vacuum fractional distillation over zinc dust as described by Sebastian et al. (*1*). Samples from the condensates of both the overhead and the bottom cell effluents were analyzed by gas chromatography. The analysis indicated small amounts of impurities in the condensate from experiments at 703 K. The impurities were probably isoquinoline. However, the sum of the peak areas of these impurities never amounted to more than 1.5% of the total peak area of the sample at any of the conditions studied. All recycled quinoline was purified before reuse.

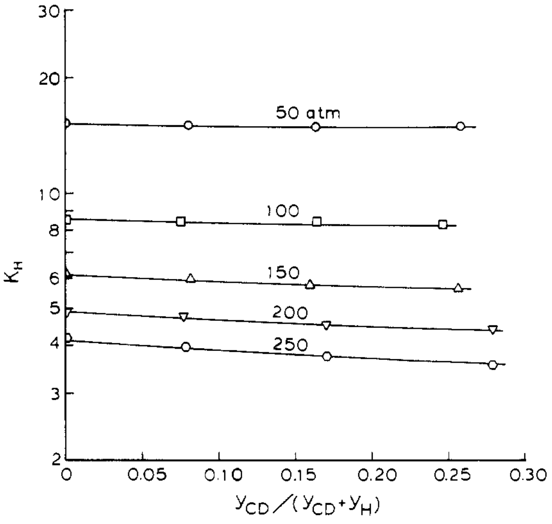

Figure 1. *K* values of hydrogen at 703 K.

Matheson primary standard mixtures of hydrogen and carbon dioxide at carbon dioxide compositions of 0.997, 9.932, 25.017, and 49.749 mol % were used for the calibration of the gas chromatograph. The calibration was checked daily during the course of this work.

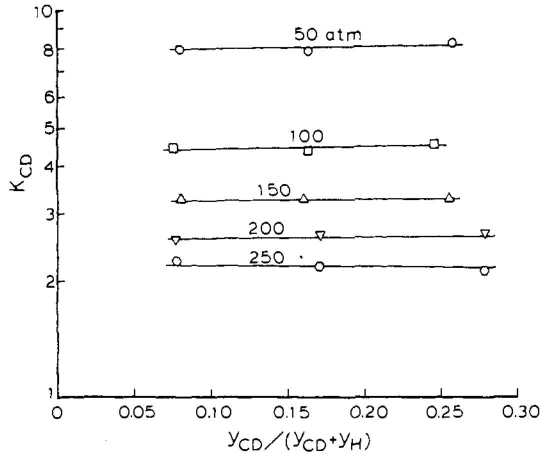

Figure 2. *K* values of carbon dioxide at 703 K.

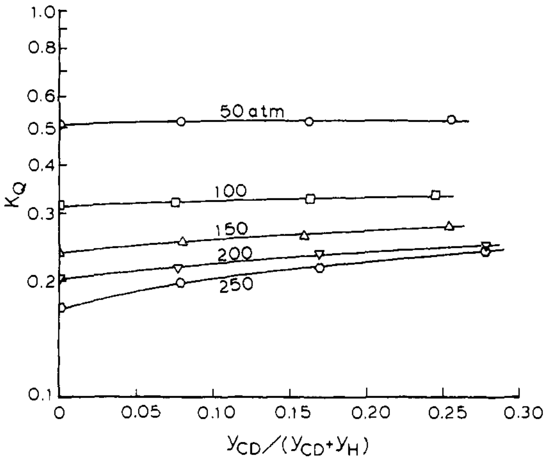

Figure 3. *K* values of quinoline at 703 K.

Results and Discussion

Equilibrium phase compositions were experimentally determined at two temperatures, 543 and 703 K, over a pressure range from 50 to 250 atm. The results are tabulated in Table I. Also shown in the table are the feed gas compositions. Measurements were made at three feed gas concentrations at ca. 75, 84, and 92 mol % hydrogen, at each condition of *T* and *p*.

The data reported in the table are the averages of multiple samples. At least two samples were taken from each of the cell effluents at a fixed temperature, pressure, and feed gas composition. The compositions of the multiple samples generally agreed to within 1.5%.

The response of the *K* values to variation in the gas compostion is illustrated in Figures 1–3, which show the *K* values of hydrogen, carbon dioxide, and quinoline, respectively, as a function of quinoline-free mole fraction of carbon dioxide in the equilibrium gas at 703 K. The end points at $y_{CD} = 0$ shown in Figures 1 and 3 correspond to binary mixtures of hydrogen + quinoline and were taken from Sebastian and co-workers (*1*). The *K* values of hydrogen and carbon dioxide appear to be relatively insensitive to variation of gas compositions, while the effect of changing compositions on the *K* values of quinoline is significant at higher pressures. Similar results were observed at 543 K.

Glossary

K	vaporization equilibrium ratio, y/x
p	pressure, atm
T	temperature, K
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

CD	carbon dioxide
H	hydrogen
Q	quinoline

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