the same coordinates. Figure 3 shows plots of the selectivity $\beta_{C,A} = X_{CB}X_{AA}/X_{AB}X_{CA}$ vs. $x_2/x_1 = (X_{AA}X_{BB}/X_{BA}X_{AB})^{1/2}$. (The physical meaning of x_2/x_1 is discussed in ref *2*.) The dependence of the solubility on temperature is shown clarly in these figures.

Glossary

X_{AB}	liquid weight fraction of A in the B-rich phase
x_2/x_1	the quantity defined by $(X_{AA}X_{BB}/X_{BA}X_{AB})^{1/2}$
$\beta_{C,A}$	selectivity of B for C from an A-C solution

Subscripts

A	component (diluent, cyclohexane)
B	component (solvent, ammonia)
C	component (solute, cyclohexene)

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Vapor-Liquid Equilibria of the Water-Ethanol System at Low Alcohol Concentrations

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Vapor-liquid equilibrium data for the ethanol-water system at 760 mmHg are collected by using a Gillespie-type still. Data in the range of ethanol concentration from 0.01 to 1.0 wt % are scarce, and yet they are much needed in the design of efficient ethanol recovery systems.

There has been strong interest in the use of renewable energy to reduce the consumption of petroleum fuel. An important consideration in biomass conversion concerns the energy consumption needed to produce alcohol compared to the energy content of the final alcohol product. Hence, there is a special interest in reducing energy consumption in the ethanol recovery step since it consumes a significant portion of the energy of the overall process. In low-energy distillation modeling, the bottom product stream is often assumed to contain no more than 0.02 wt % ethanol (*1*, *2*). This constraint implies the requirement of efficient stripping. Otherwise, this alcohol loss becomes a significant cost factor when the feed concentration is low. In fact, low alcohol concentrations of 6-8 wt % ethanol are commonly encountered in the fermentation beer stream fed to a distillation system in the manufacture of fuel alcohol. How one can recover alcohol from a very dilute aqueous solution has thus became increasingly important as the interest in fuel alcohol further develops.

Approximately 80 reports have appeared in the literature since 1895 on the vapor-liquid equilibrium data of the ethanol-water system (*3*). However, these investigations have seldom been performed at concentrations lower than 1 wt % ethanol. Specifically, only the report by Dalager (*4*) contains data at concentrations between 0.01 and 0.1 wt % ethanol (four data points with concentrations between 0.038 and 0.053 wt % ethanol). In this paper, extensive vapor-liquid equilibrium data are reported for ethanol concentrations of 0.01-1.0 wt %.

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Experimental Methods and Materials

Apparatus. An equilibrium still designed on the principle of the Gillespie still (*5*) was used. Figure 1 shows the apparatus, which was built mainly of Pyrex glass and consisted of a mixture reservoir, a still, a disengagement vessel, a condensate collector, and a cottrell tube connecting the disengagement vessel to the still. The still is a concentric tube surrounded by heating tape. The boiling rate of the mixture in the outer shell of the tube was controlled by heat input through the heating tape. The cottrell tube and the disengagement vessel were insulated from the surroundings by glass wool. The tip of the thermocouple in the disengagement vessel was located at the end of the cottrell tube. To prevent condensation of the atmospheric moisture through the condenser, a Drierite container was attached to the condenser.

All experiments were run at atmospheric pressure (760 mmHg). The temperatures were measured with an alumel-chromel thermocouple and displayed on a digital thermometer (Omega Engineering, Inc., Stamford, CT 06907). The measurements were made to 0.2 °C accuracy. The determinations of the ethanol concentrations were done by gas chromatography, refractive index, or a Karl Fischer-type water analyzer depending on the concentration range. The concentrations in the range of 0.01~2 wt % were measured by gas chromatography (Model 311, Carle Instruments, Inc., Anaheim, CA 92801) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The concentrations in the range of 2~20 wt % were measured by a refractometer (Abbe 3L, Baucsh & Lomb, Rochester, NY 14625). The concentrations above 20 wt % were determined by a Karl Fischer water analyzer (Aquatest-IV, Photovolt Corp., New York, NY 10010). The column (stainless, 87 cm long, 0.635 cm o.d, 0.319 cm i.d) used for gas chromatography was packed with pure cellulose (Avicel PH-101, Lot 1645, FMC Corp., Marcus Hook, PA 19061) which is capable of the separation of ethanol and water (*6*). The column was thermostated at 150 °C in an oven. Helium, hydrogen, and air were used as carrier gas, fuel,

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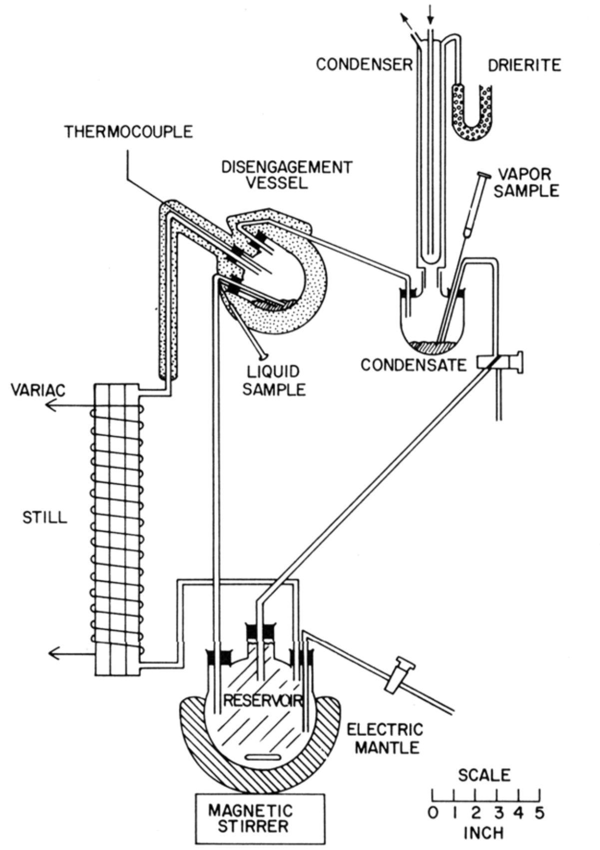

Figure 1. Schematic diagram of apparatus used in equilibrium study.

Table I. Vapor-Liquid Equilibrium Data for Ethanol-Water at 760 mmHg

liquid		vapor					
wt % EtOH	mol % EtOH	wt % EtOH	mol % EtOH	K_{EtOH}	K_{H_2O}	γ_{EtOH}	γ_{H_2O}
0.016	0.0063	0.23	0.090	14.3	0.999	6.65	0.999
0.019	0.0074	0.24	0.094	12.7	0.999	5.90	0.999
0.019	0.0074	0.23	0.090	12.2	0.999	5.67	0.999
0.022	0.0086	0.25	0.098	11.4	0.999	5.30	0.999
0.022	0.0086	0.28	0.110	12.8	0.999	5.95	0.999
0.023	0.0090	0.28	0.110	12.2	0.999	5.67	0.999
0.023	0.0090	0.29	0.114	12.7	0.999	5.90	0.999
0.026	0.0102	0.28	0.110	10.8	0.999	5.02	0.999
0.028	0.0109	0.40	0.157	14.4	0.999	6.69	0.999
0.029	0.0113	0.34	0.133	11.8	0.999	5.49	0.999
0.033	0.0129	0.35	0.137	10.6	0.999	4.93	0.999
0.047	0.0184	0.60	0.235	12.8	0.998	5.95	0.998
0.048	0.0188	0.60	0.235	12.5	0.998	5.81	0.998
0.058	0.0227	0.64	0.251	11.1	0.998	5.16	0.998
0.062	0.0242	1.07	0.421	17.4	0.996	8.01	0.996
0.073	0.0285	0.91	0.358	12.6	0.997	5.86	0.997
0.074	0.0289	0.79	0.310	10.7	0.997	4.97	0.997
0.075	0.0293	0.92	0.362	12.4	0.997	5.76	0.997
0.080	0.0313	0.97	0.381	12.2	0.997	5.67	0.997
0.095	0.0371	1.05	0.413	11.1	0.996	5.16	0.996
0.18	0.070	1.96	0.775	11.1	0.993	5.16	0.993
0.19	0.074	1.51	0.596	8.05	0.995	3.74	0.995
0.30	0.117	2.43	0.964	8.24	0.992	3.83	0.992
0.34	0.133	2.41	0.956	7.09	0.992	3.30	0.992
0.40	0.156	3.21	1.28	8.21	0.989	3.82	0.989
0.43	0.168	3.50	1.40	8.33	0.988	3.87	0.988
0.61	0.238	4.22	1.69	7.10	0.985	3.30	0.985
0.61	0.238	4.14	1.66	6.97	0.986	3.24	0.986
0.62	0.242	5.20	2.10	8.68	0.981	4.03	0.981
0.73	0.285	5.23	2.11	7.40	0.982	3.44	0.982

and oxidant, respectively. The outputs from the TCD and FID were monitored by a two-pen Model 7100 Hewlett-Packard strip chart recorder (Hewlett-Packard, San Diego, CA 92127). Deionized water and anhydrous ethanol (USP, U.S. Industrial Chemicals Co., New York, NY 10016) were used to make up the solutions used in the equilibrium studies. The accuracies of the concentration measurements by gas chromatography, refractometer, and Karl Fischer water analyzer were determined to be 0.0005, 0.05, and 0.05 wt % ethanol, respectively.

Procedure. Known concentrations of aqueous ethanol were charged to the reservoir and the still until the liquid level reached the top of the still. At this time, heating of the reservoir and the still was initiated. To minimize the time required for attaining equilibrium, an electric mantle was used to heat the reservoir

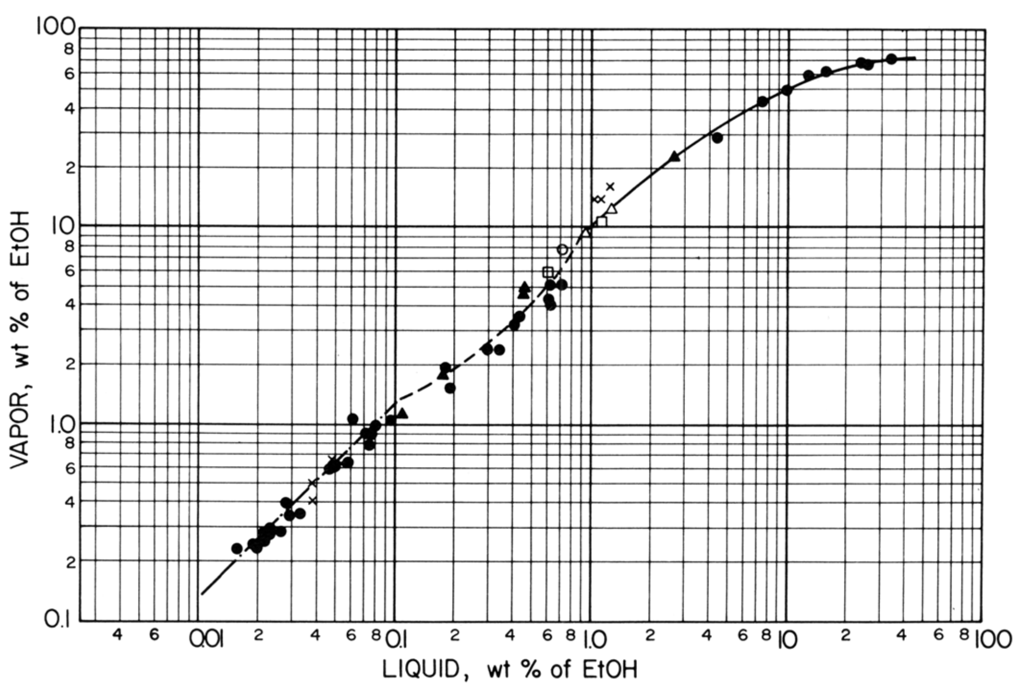

Figure 2. Vapor–liquid equilibrium for ethanol–water at 760 mmHg: (●) this work; (×) Dalager (*4*); (▲) Altsheler et al. (*7*); (□) Cornell and Montonna (*8*); (○) Rieder and Thompson (*9*); (△) Otsuki and Williams (*10*). The solid line for the range of concentration of 1–50 wt % in the liquid phase represents smoothed data from previous reports (*4*, *8–16*). The line (– – –) for the range of concentration of 0.1–1.0 wt % represents smoothed data from previous reports (*7–10*) and this work. The straight line (–•–) for 0.01–0.1 wt % is drawn with averaged *K* value (12.4).

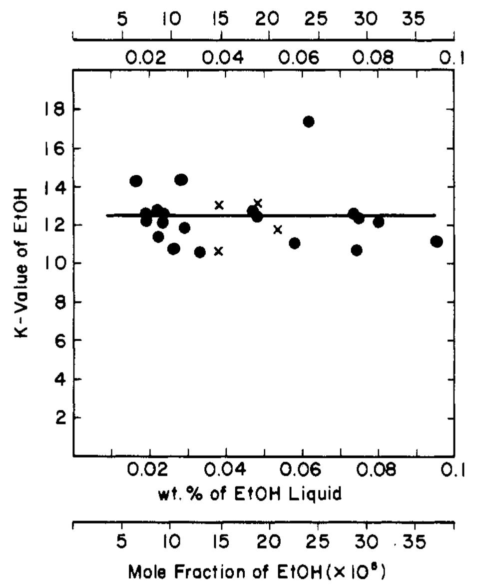

Figure 3. *K* value vs. mole fraction of EtOH: (●) this work; (X) Dalager (4); (—) averaged *K* value with data of this work (12.4).

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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