G^E/RT	dimensionless excess Gibbs free energy
k_{12}	interaction constant
P	pressure, bar
R	gas constant
T	temperature, K
v	molar volume, cm^3/mol
x_i	liquid-phase mole fraction
y_i	vapor-phase mole fraction
γ_i	liquid-phase activity coefficient
Λ_{12}, Λ_{21}	parameters of the Wilson equation
ϕ_i	vapor-phase fugacity coefficient
Ω_a, Ω_b	dimensionless constants in the modified Redlich-Kwong equation of state

Subscripts

c	critical
i	component i
j	component j
1	CF_4
2	$CClF_3$

Superscripts

l	liquid
°	standard state
s	saturation

Literature Cited

(1) Stein, F. P., Sterner, C. J., Geist, J. M., *Chem. Eng. Prog.*, **58** (11), 70 (1962).
(2) Stein, F. P., Proust, P. C., *J. Chem. Eng. Data*, **16**, 389 (1971).
(3) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1969, pp 212, 157, 229.
(4) Chueh, P. L., Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, **6**, 492 (1967).
(5) Gupta, V. K., M.S. Thesis, Lehigh University, Bethlehem, Pa., 1970.
(6) Freon Products Division, E. I. du Pont de Nemours and Co., "Preliminary Thermodynamic Properties of Freon-14 Fluorocarbon", Technical Bulletin T-14 (1961).
(7) Freon Products Division, E. I. du Pont de Nemours and Co., "Freon-13 Refrigerant Thermodynamic Properties", Technical Bulletin T-13A (1967).
(8) Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).
(9) Reid, R. C., Prausnitz, J. M., Sherwood, T. K., "The Properties of Gases and Liquids", 3rd ed., McGraw-Hill, New York, 1977, p 315.

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Vapor-Liquid Equilibria in Hydrogen + 9,10-Dihydrophenanthrene Mixtures

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Saturated fluid-phase compositions at vapor-liquid equilibrium were experimentally determined for hydrogen + 9,10-dihydrophenanthrene mixtures at temperatures of 188.3, 269.0, 349.7, and 429.9 °C over the pressure range of 20-250 atm.

Introduction

Vapor-liquid equilibrium data for mixtures of hydrogen and hydrocarbons are needed for engineering design of hydrotreating and hydrogenation processes. Data are especially needed at elevated temperatures and pressures. In this study we report experimentally observed saturated equilibrium phase compositions and K values for the system hydrogen + 9,10-dihydrophenanthrene at conditions of industrial interest. The equilibrium phase behavior of this mixture system has not been previously reported in the literature.

Experimental Section

The experimental apparatus and procedure used in this study have been described (*1-3*).

Hydrogen gas was supplied by Airco with a minimum purity of 99.95% and was directly used without further purification. 9,10-Dihydrophenanthrene was purchased from Aldrich Chemical Co. with a reported purity of 97%. Before being used in this study it was zone refined to recover the colorless sections. The remaining colored portion from the zone refiner was fractionally distilled under a nitrogen blanket at a reduced pressure. The distillate was combined with the colorless sections from the zone refiner for use as feed to the equilibrium apparatus. The purity of this combined feed was found to be 99+% from gas chromatographic analysis.

Dihydrophenanthrene samples were taken from the cell effluents in all experimental runs and were analyzed by gas chromatography to test for possible thermal decomposition. No appreciable chemical change was detected at the three lower temperatures of the reported experiments. However, phenanthrene was found to be present to the extent of about 4-5% of the dihydrophenanthrene in the samples of the 430 °C runs. The reported mole fractions of dihydrophenanthrene at 430 °C include those of phenanthrene. We report the data at 430 °C in spite of the known chemical changes in the belief that equilibrium conditions are not substantially altered in view of the closely similar properties of phenanthrene and dihydrophenanthrene. It is, nevertheless, clear that the data at 430 °C are less accurate than the data at the lower temperatures.

Results

Compositions of equilibrium saturated vapor and liquid phases of hydrogen + 9,10-dihydrophenanthrene mixtures were determined at four temperatures, 188.3, 269.0, 349.7, and 429.9 °C, at seven pressures from 20 to 250 atm. The results are summarized in Table I. The phase compositions reported in the table represent the mean of duplicate samples. Individual samples are shown in Figures 1 and 2 as separate points when they can be distinguished. Saturated liquid compositions at all the four observed temperatures are shown in Figure 1, but the saturated gas compositions are shown in Figure 2 for only the two higher temperatures. The saturated gas phases are essentially all hydrogen at the lower temperature isotherms and could not be meaningfully presented in Figure 2.

Also tabulated in Table I are the equilibrium ratios of hydrogen and dihydrophenanthrene. These values were obtained from the averaged x's and y's. Figure 3 shows the K values of hydrogen as a function of pressure while Figure 4 shows the

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Table I. Hydrogen + 9,10-Dihydrophenanthrene Gas-Liquid Equilibrium Data

p, atm	x_H	y_H	K_H	K_D
		188.3 °C		
19.42	0.0093	0.997 76	107.29	0.002 26
30.31	0.0141	0.998 60	70.82	0.001 420
49.56	0.0231	0.999 20	43.26	0.000 819
99.78	0.0446	0.999 57	22.41	0.000 450
150.3	0.0649	0.999 64	15.40	0.000 385
201.0	0.0843	0.999 73	11.86	0.000 295
252.1	0.1032	0.999 71	9.69	0.000 323
		269.0 °C		
20.11	0.0126	0.979 6	77.75	0.020 7
29.97	0.0191	0.986 4	51.64	0.013 86
49.64	0.0308	0.991 6	32.12	0.008 67
99.31	0.0595	0.995 3	16.73	0.005 00
150.1	0.0868	0.996 7	11.48	0.003 61
200.1	0.1139	0.997 1	8.75	0.003 27
248.3	0.1374	0.997 4	7.26	0.003 01
		349.7 °C		
20.17	0.0156	0.899 2	57.64	0.102 4
29.87	0.0233	0.930 6	39.94	0.071 1
47.12	0.0375	0.954 8	25.46	0.047 0
100.5	0.0769	0.976 9	12.70	0.025 0
150.1	0.1121	0.983 4	8.77	0.018 7
202.7	0.1462	0.986 7	6.75	0.015 7
250.7	0.1720	0.988 8	5.75	0.013 5
		429.9 °C		
19.95	0.0161	0.650 0	40.37	0.355 7
29.84	0.0280	0.759 7	27.13	0.247 2
49.71	0.0492	0.849 7	17.27	0.158 7
100.2	0.0984	0.919 1	9.34	0.089 7
150.7	0.1446	0.944 3	6.53	0.065 1
200.7	0.1815	0.957 5	5.28	0.051 9
249.4	0.2184	0.962 9	4.41	0.047 5

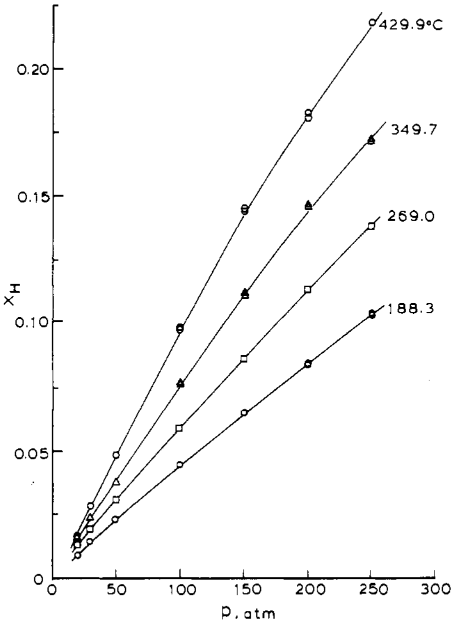

Figure 1. Solubility of hydrogen in 9,10-dihydrophenanthrene.

K values of dihydrophenanthrene.

Glossary

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

Subscripts

H	hydrogen
D	9,10-dihydrophenanthrene

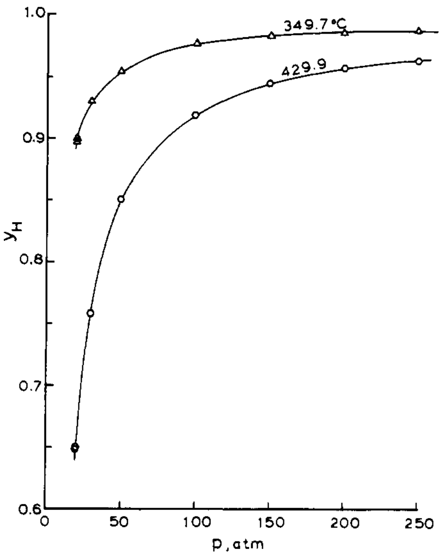

Figure 2. Mole fraction of hydrogen in saturated gas.

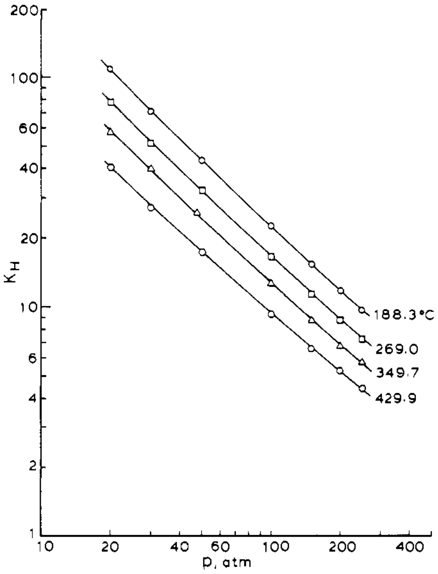

Figure 3. *K* values of hydrogen.

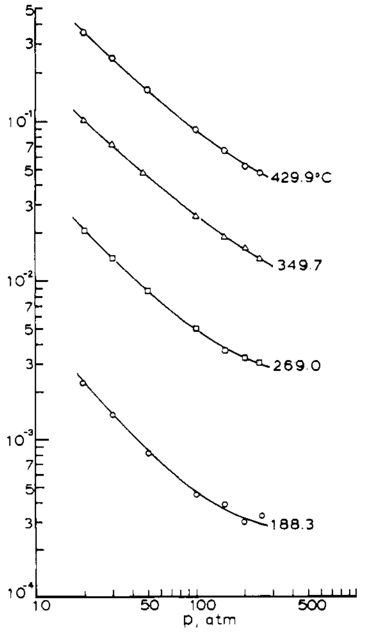

Figure 4. *K* values of 9,10-dihydrophenanthrene.

Literature Cited

(1) Simnick, J. J., Lawson, C. C., Lin, H. M., Chao, K. C., *AIChE J.*, **23**, 469 (1977).
(2) Simnick, J. J., Liu, K. D., Lin, H. M., Chao, K. C., *Ind. Eng. Chem. Process Des. Develop.*, **17**, 204 (1978).
(3) Yao, J., Sebastian, H. M., Lin, H. M., Chao, K. C., *Fluid Phase Equilib.* **1**, 293 (1978).

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Adsorption of Aliphatic Acids from Aqueous Solutions onto Activated Carbon

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The radioisotope technique was applied to study the removal of aliphatic acid contaminants found in byproduct waters of fossil fuel conversion processes at three different temperatures. Five pure component systems (acetic acid, propionic acid, *n*-butyric acid, *n*-hexanoic acid, and *n*-heptanoic acid) were investigated at three different temperatures, 278, 298, and 313 K, by using activated carbon as the adsorbent. The results were modeled by a three-parameter adsorption isotherm equation.

Introduction

In recent years, the adsorption of organic contaminants from aqueous solution was studied primarily by chromatographic techniques and the uptake was calculated from the invariant adsorption equation (*3*, *8*). Several different systems have been reported for different adsorbents at different temperatures (*1*–*4*, *6*, *7*, *9*–*13*). However, only a few systems have been studied over wide concentration ranges. Among those works mentioned above, Hansen et al. (*3*), Hansen and Craig (*2*), Linner and Gortner (*4*), and Parkash (*6*) presented experimental data for the adsorption of aliphatic acids on various types of activated charcoal over moderate concentration ranges. This study presents the adsorption data of five carboxylic acids at three different temperatures obtained over a wide concentration range by using radioactive tracer techniques. Analytical sensitivity can be improved by the use of radioactive tracer techniques with an expected 10^3–10^6 increase in sensitivity over conventional spectroscopic or chromatographic quantitation methods (*5*). The amount of uptake can be determined by counting the radioactivity of the solution after the equilibrium is reached. Neither the assumption of very dilute solution in using the invariant adsorption equation (*7*, *14*) nor the surface excess calculation (*12*) is needed when using this method. The data obtained are important for developing theoretical adsorption models applicable to wide concentration ranges.

Experimental Section

The major experimental apparatus used in this study was a Beckman Instrument Co. liquid scintillation counter, Model LS-9000. All of the organic acids were obtained from Pfaltz Bauer, Inc. The purities were 99+% as determined by a chromatographic analysis. Radioactive acetic acid, propionic acid, and *n*-butyric acid were obtained from the Radiochemical Center, Amersham, England, whereas *n*-hexanoic acid and *n*-heptanoic acid were obtained from ICN Pharmaceutical, Inc. The lignite-based activated carbon was obtained from Darco Co., Denver, Col. A 20 × 40 mesh material with a total surface area of 667 m^2/g was used.

According to the report from the manufacturer, the activated carbon was washed by a strong acid to leach out undesirable inorganics such as calcium, magnesium, iron, and aluminum. This was followed by water washing until the water extract reached a pH of 6. The activated carbon was further cleaned for this study by washing with double distilled water until no flocculation was seen. Then the washed activated carbon was heated at 428 K for 9 h. The same procedures were repeated twice before taking adsorption data. The concentrations of acetic, propionic, and *n*-butyric acids varied from 1 to 5000 ppm. The concentration of *n*-hexanoic acid varied from 100 to 2500 ppm, and the concentration of *n*-heptanoic acid varied from 100 to 2000 ppm.

The radioanalytical approach used in these adsorption experiments involved the addition of a small mass (less than 1 μg) of high specific activity radioactive solute to each of the stock solutions of solute made up at varying concentrations. This imparted a uniform and high solute specific activity to each of the stock solutions with negligible change to the final solute concentration. This method provides an equally sensitive and accurate radioanalysis for determining solute concentrations at both high and low levels. The net result is that the overall statistical variance and accuracy of the results obtained are the same over the entire concentration range.

After preparing the radioactive solutions, samples of 5 mL were taken before and after equilibration with the activated carbon. The radioactivity was counted after mixing 1 mL (out of 5 mL) of each sample with 12 mL of Dimilume-30, Packard Instrument Co. Ninety-five milliliters of each sample solution was shaken with 0.5 g of activated carbon in a shaker bath set at either 278, 298, or 313 K, for 48 h to reach equilibrium. Samples were placed in the liquid scintillation counter and dark adapted for at least 30 min prior to counting. Counting was performed in a wide open ^{14}C window and continued until a 2σ count rate error of 0.1% or less was achieved. Random coincidence monitoring was used to ensure that the contribution of counting events not due to radioactivity disintegrations, e.g., chemiluminescence, was less than 0.2%. The counting efficiency was determined for each sample and was used to compute the absolute activity as disintegrations per minute (DPM). Efficiency corrections were made by instrumental measurement of the Compton edge inflection point (a Beckman modification

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