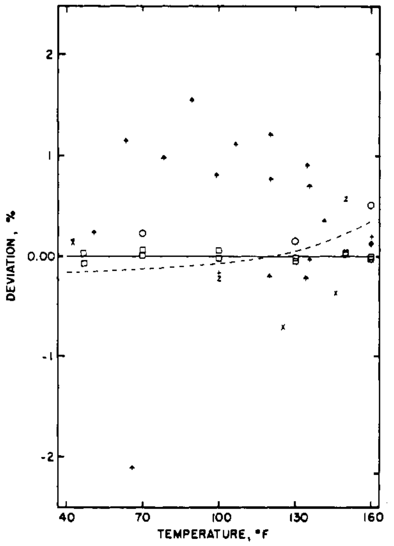

Figure 3. Literature study of *n*-butane: □, raw experimental data of this study; O, Sage et al., 1937 (*15*); +, Olds et al., 1944 (*13*); X, Kay, 1940 (*9*); ↑, Data et al., 1926 (*7*); X̄, Wackher et al., 1945, (*19*); Z, Laurance and Swift, 1974 (*10*); ◇, Connolly, 1962 (*6*); Δ, Hirata et al., 1969 (*8*); --, A.P.I. 44, 1974 (*2*).

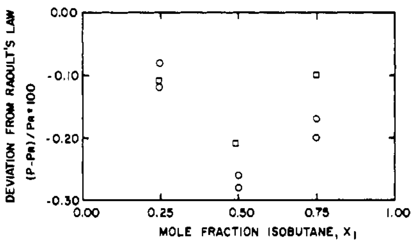

Figure 4. Comparison of deviation from Raoult's law for isobutane (1)-*n*-butane (3) at 160 °F: O, this study; □, Connolly, 1962 (*6*).

temperature range of 40 to 160 °F with an estimated average accuracy of 0.04%. These data are suitable for use in the design of distillation equipment for the separation of C_4 hydrocarbons and should also be useful in analyzing the molecular interactions between paraffin and olefin hydrocarbons.

Glossary

A, B, C	constants (Antoine constants) for eq 1
P	pressure, psia
T	temperature, °F
x	liquid-phase composition
z	overall composition
σ_p	standard deviation for pressure, psi

Subscripts

calcd	calculated with eq 1
1	component identification: 1 = isobutane, 2 = isobutylene, 3 = *n*-butane
P	with respect to pressure
R	pressure calculated by Raoult's law, psia

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Gas-Liquid Equilibrium of the Hydrogen/Bicyclohexyl System at Elevated Temperatures and Pressures

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Vapor-liquid equilibrium data are determined for the system hydrogen/bicyclohexyl at four temperatures from 190 to 430 °C and seven pressures up to 250 atm in a flow type apparatus. Attainment of equilibrium was checked by varying input flow rates and checking the thermodynamic consistency of the data by integration of the Gibbs-Duhem equation. The new data are compared with general correlations in the literature.

Introduction

Recently there has been an increased interest in vapor-liquid equilibrium data involving H_2/hydrocarbon systems at elevated temperatures and pressures in response to the development of coal liquefaction and hydrotreating processes. Such information is useful not only for the engineering design of gas-liquid contacting and separation equipment but also for the study of reaction kinetics in coal liquefaction mixtures.

Work in this laboratory has been concerned with gas-liquid

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equilibrium in mixtures of hydrogen and heavy hydrocarbons typically found in coal derived liquids. Simnick et al. (*11*, *12*) reported on hydrogen/tetralin and hydrogen/diphenylmethane mixtures; Yao et al. (*13*) reported on hydrogen/1-methylnaphthalene. The present work investigates the phase behavior of the system hydrogen/bicyclohexyl at four temperatures from 190 to 430 °C and seven pressures from 20 to 250 atm. A review of prior literature concerning hydrogen/hydrocarbon systems at elevated temperatures and pressures was made by Simnick et al. (*11*).

Apparatus

The apparatus used in this work has been previously described by Simnick et al. (*11*). Briefly, the system is of the flow type to reduce the residence time of the fluids in the high-temperature equilibration zone. All parts of the apparatus exposed to high temperature and pressure are made of stainless steel type 316.

The hydrogen gas, which is supplied to the system either directly from a high-pressure gas cylinder or through a Höfer compressor, and the liquid feed, which is delivered from a Hills-McCanna U-type metering pump, are joined at a tee. The two-phase mixture is heated in a tube 3.3 m long, the last 1.2 m of which is fitted with a notched spiral ribbon to promote mixing. The rate of heating is controlled so that the temperature of the feed stream, measured at the inlet to the cell by an Autoclave sheath-type thermocouple, is within 1 °C of the cell temperature. The temperature of the feed at the inlet to the cell fluctuates no more than 0.7 °C during a run.

The feed mixture then flows into the equilibrium cell, where the gas and liquid phases are separated.

The cell temperature is measured with a calibrated Type-K chromel alumel thermocouple. The cell temperature fluctuates within 0.1 °C during a run.

The cell pressure is measured by a Heise gauge that reads pressures up to 340 atm and is accurate to 0.1% or 0.3 atm whichever is the greater.

The liquid and gas streams from the cell are cooled and reduced in pressure and then fed to a common separator to remove the hydrogen, which is then vented to the atmosphere. The bicyclohexyl from the separator can be either recycled to the feed pot or taken off for purification before reuse.

Samples are diverted from the cell effluents after they are reduced in temperature and pressure before they enter the separator. The diverted stream enters a trap where the condensate is retained and later removed for weighing. The quantity of gas leaving the traps is determined volumetrically. For samples of the overhead from the equilibrium cell the volume is measured using a wet test meter. For samples of the bottom product the gas is collected in graduated cylinders over water. These volume determinations are accurate to ±0.5%.

Due to the enormous difference in volatilities of hydrogen and bicyclohexyl at ambient conditions, nearly complete separation is obtained at the liquid trap. The amount of bicyclohexyl in a sample is the sum of that in the weighed liquid and the relatively small amount which remains in the vapor at room temperature. The latter is accounted for using vapor pressure data of bicyclohexyl by Dobry and Keller (*5*). The amount of hydrogen in a sample is the sum of that in the gas phase plus that dissolved in the liquid. The hydrogen dissolved in the liquid is found from Henry's law using values of the Henry constant reported by Cukor and Prausnitz (*4*).

To determine possible effects of flow rate on composition several samples were taken at the same conditions of temperature and pressure but differing liquid flow rates between 500 and 2000 mL/h. No appreciable differences in sample compositions were found. The gas flow rate was maintained at about 5.5 L/min measured at ambient conditions. Depending on the pressure, temperature, and flow rates, the plug flow residence time of the solvent in the cell was between 12 and 33 s.

Table I. Vapor-Liquid Equilibrium Data for H_2/Bicyclohexyl

p, atm	x_H	y_H	K_H	K_B
		189.0 °C		
20	0.0181	0.9842	54.4	0.01611
30	0.0262	0.9889	37.7	0.01143
50	0.0443	0.9929	22.4	0.00743
100	0.0810	0.9958	12.29	0.00453
150	0.1158	0.9969	8.61	0.00351
200	0.1418	0.9974	7.03	0.00303
250	0.1718	0.9977	5.81	0.00277
		268.7 °C		
20	0.0212	0.8988	42.4	0.1034
30	0.0329	0.9312	28.3	0.0712
50	0.0543	0.9558	17.60	0.0467
100	0.1031	0.9748	9.45	0.0281
150	0.1480	0.9813	6.63	0.0220
200	0.1899	0.9845	5.18	0.0191
250	0.2268	0.9866	4.35	0.0174
		348.6 °C		
20	0.0211	0.6117	29.0	0.397
30	0.0382	0.7322	19.16	0.278
50	0.0686	0.8296	12.09	0.1829
100	0.1398	0.9060	6.48	0.1093
150	0.1975	0.9298	4.71	0.0875
200	0.2578	0.9445	3.66	0.0747
250	0.3112	0.9533	3.06	0.0677
		428.5 °C		
20	0.0054	0.0602	11.15	0.945
30	0.0289	0.2463	8.52	0.776
50	0.0793	0.4885	6.16	0.555
100	0.1818	0.6720	3.70	0.400
150	0.2680	0.7467	2.79	0.346
200	0.3494	0.7857	2.25	0.330
250	0.4239	0.8050	1.90	0.339

Materials

The hydrogen gas used in this study was obtained from Air Products Co. with a reported purity of 99.95%. The bicyclohexyl was obtained from Fisher Scientific Co. with a grade of "highest purity" and a reported mp range of 3–4 °C. Gas chromatographic analysis showed one impurity amounting to about 1 mol %. Samples of the bicyclohexyl were taken from the condensate of the cell effluents at all conditions. Gas chromatographic analysis of the samples showed about 2–3% impurities. These samples also showed a slight yellow coloration. All bicyclohexyl from the cell effluents was therefore distilled at reduced pressure under a nitrogen blanket after each use to remove these impurities. After distillation the bicyclohexyl was as pure as purchased.

Results

Table I shows the equilibrium of saturated gas and liquid compositions and K values. The entries in this table represent average values obtained from duplicate samples. The mole fractions of hydrogen of the duplicates generally agreed within 1%.

Henry's constant, H, is defined by

$$H = \lim_{x \to 0} f/x$$

The values for H_2 in bicyclohexyl determined in this work are shown in Table II. These values were determined by extrapolating a plot of f_H/x_H to $x_H = 0$ where the fugacity of f_H was calculated from the Prausnitz and Chueh (*8*) modified Redlich-Kwong equation of state. The physical properties of bicyclohexyl needed in the calculations are given in Table III. An interaction constant was used in the equation and the value

Table II.

Temp, °C	Henry constant, atm	Temp, °C	Henry constant, atm
189.0	1040	348.6	587
268.7	825	428.5	375

Table III. Physical Properties of Bicyclohexyl

T_c	731.4 K	ω	0.388
P_c	25.3 atm	δ	8.7 (cal/mL)$^{1/2}$
$\tilde{V}_c$	577 mL/g-mol	$\tilde{V}$ (25 °C)	187.7 mL/g-mol

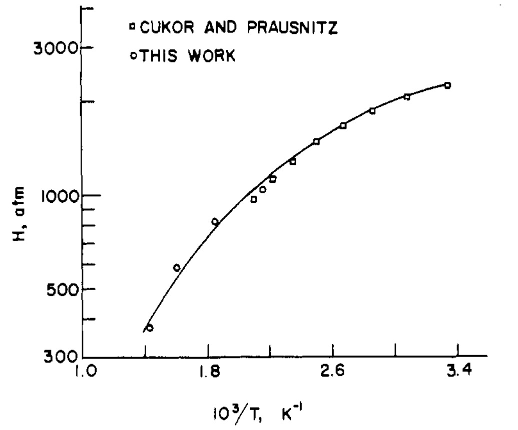

Figure 1. Henry's constant of hydrogen in H_2/bicyclohexyl.

was estimated by the procedure described by Yao et al. (*13*). Figure 1 shows a comparison of the Henry constant values from this work with those from Cukor and Prausnitz (*4*) determined from low-pressure data collected in a glass apparatus. The results appear to be in reasonable agreement.

Thermodynamic Consistency

The data were tested for thermodynamic consistency by use of the Gibbs-Duhem equation integrated by the method of orthogonal collocation (*3*, *13*). In this test the Gibbs-Duhem equation is integrated to give the equilibrium vapor composition from the experimental isothermal pressure and liquid composition data. The calculated vapor compositions are compared to the experimental values to determine whether or not the data are thermodynamically consistent.

In addition to isothermal p-x data three quantities are required to be known for the application of this method: the vapor pressure of the solvent, the excess volume of the liquid solution, and the fugacity coefficients of the vapor mixture.

Vapor pressure data on bicyclohexyl were taken from Dobry and Keller (*5*). The fugacity coefficients were determined from the Prausnitz and Chueh (*8*) modified Redlich-Kwong equation of state. The excess volume of the liquid solution was determined by using the method of Prausnitz and Chueh for the molal volume of the solution and for the partial volume of bicyclohexyl, while the partial molal volume of hydrogen was determined by using the correlation of Brelvi and O'Connell (*1*).

The comparison of the vapor composition calculated by the orthogonal collocation method with the experimental data at 189 °C is shown in Figure 2. Only this isotherm is calculated since it is the only temperature we studied at which the vapor pressure of bicyclohexyl is known.

Vapor pressures have been determined in the past with the same vapor-liquid equilibrium apparatus described here. However, no valid vapor pressure values were obtained in this work for bicyclohexyl due to appreciable chemical reactions at the temperatures of interest. Hydrogen apparently acts as an inhibitor for these reactions and in the absence of hydrogen during the vapor pressure experiment the reaction took place. Reactions are also favored by the increased residence time of the liquid in the heater in the absence of hydrogen.

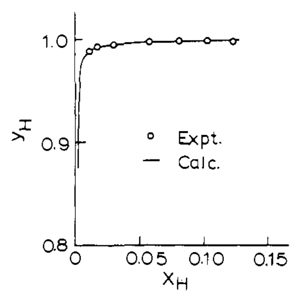

Figure 2. Comparison of orthogonal collocation calculations with experimental results at 189 °C.

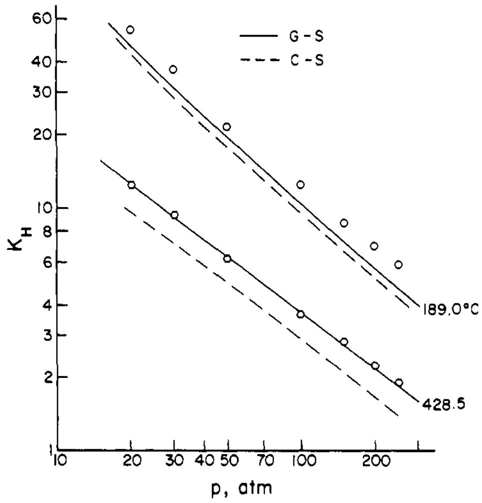

Figure 3. Comparison of K_H data in H_2/bicyclohexyl with correlations.

The agreement shown in Figure 2 suggests that the present data are thermodynamically consistent and represent equilibrium conditions. The latter observation is supported by the satisfaction of the thermodynamic consistency test by the data on other mixture systems determined in this apparatus at similar conditions (*11*, *12*, *13*).

Comparison with Correlations

The Chao-Seader correlation (*2*) for vapor-liquid equilibrium data has been in use. Their results for hydrogen have been found to agree well with data up to pressures above the highest of this study, but the temperature must be limited to below 260 °C due to the lack of a data base at higher temperatures. Nonetheless, use of the correlation has persisted at higher temperatures.

Grayson and Streed (*6*) extended the Chao-Seader correlation to higher temperatures by modifying the equations for pure liquid fugacity based on their own data for H_2/heavy oil systems.

Comparisons of the correlations with the K values of this work are shown in Figures 3 and 4. Only the highest and lowest isotherms are shown in Figure 3 as the intermediate isotherms are similar. K values of bicyclohexyl are well represented by both correlations but the K values of hydrogen are not. The Chao-Seader deviates by up to 35% and the Grayson-Streed by up to 25%.

The Grayson-Streed correlation appears to be improved over the Chao-Seader at all conditions tested in this work, as a result of changing only the pure liquid fugacity. The comparisons indicate that there is still room for further improvement.

Use of the correlations requires knowledge of solubility parameter, molar volume, critical properties, and acentric factor. Values of these properties for hydrogen are given elsewhere (*2*); values for bicyclohexyl are estimated here. T_c and P_c were

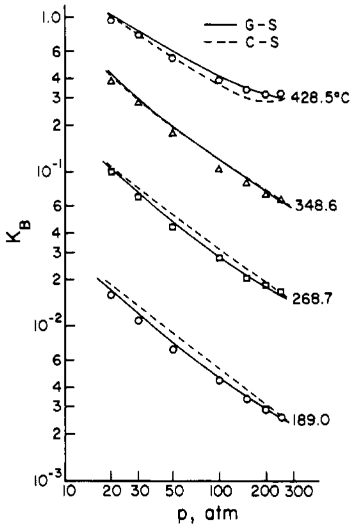

Figure 4. Comparison of K_B data in H_2/bicyclohexyl with correlations.

estimated by the Riedel method using Lydersen's critical property increments (*9*). ω was estimated by the Edmister method (*9*). The solubility parameter was estimated from the heat of vaporization calculated from the "Hildebrand rule" (*7*). This value is in agreement with that calculated with the Giacalone equation (*9*) but is lower than the value suggested by Riddick and Bunger (*10*). Cukor and Prausnitz (*4*) reported a value of solubility parameter smaller than that used in this work. The estimated physical properties of bicyclohexyl of this work are listed in Table III.

Glossary

f_i	fugacity of component *i*, atm
H	Henry's constant, atm
K_i	vaporization equilibrium ratio ≡ y_i/x_i
p	pressure, atm
T	temperature, K
$\tilde{V}$	molar volume, mL/g-mol
x_i	mole fraction of component *i* in liquid phase
y_i	mole fraction of component *i* in gas phase
δ	solubility parameter, $(cal/mL)^{1/2}$
ω	acentric factor

Subscripts

H	hydrogen
B	bicyclohexyl
C	critical properties

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Density, Viscosity, and Surface Tension of Some Single Molten Hydrated Salts

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Viscosity and surface tension of molten $Cr(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$ and the density of $Co(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were measured as a function of temperature. The temperature coefficient of molar surface energy (Eötvös constant) is found to depend on the molecular mass of the salt. Fluidities show non-Arrhenian behavior. T_0 values computed through $\phi = A_\phi T^{1/2} \exp(-B_\phi/(T - T_{0,\phi}))$ lie close to the experimentally determined glass-transition temperatures but fail to show the same sequencial order.

Increasing interest in hydrated melts, which provide liquids involving high acidities and possessing strong supercooling and glass-forming tendencies, necessitated a systematic and multipronged physicochemical investigation of these systems.

Table I. Densities and Equivalent Volumes of Molten $Co(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$

Temp, °C	Density, g cm^{-3}	Equiv vol, cm^3 $equiv^{-1}$
	$Co(NO_3)_2 \cdot 6H_2O$	
44.5	1.7900	81.28
49.6	1.7849	81.51
53.0	1.7818	81.66
57.0	1.7779	81.84
64.0	1.7710	82.15
70.0	1.7653	82.42
78.8	1.7555	82.88
	$Zn(NO_3)_2 \cdot 6H_2O$	
39.0	1.8256	81.46
43.0	1.8211	81.66
49.0	1.8141	81.98
57.0	1.8051	82.39
64.5	1.7965	82.78
72.2	1.7873	83.21
80.0	1.7783	83.63

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