were unsatisfactory in all regions near the critical of the ternary. Adjustment of the parameters, of course, forces a better fit in the critical region, but only at the expense of a poorer fit in regions removed from the critical and in the binary systems. It was not possible to obtain a set of interaction parameters that produced a satisfactory fit to both the binary and the ternary data over all regions of pressure and temperature.

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The authors wish to acknowledge the assistance of R. D. McCarthy in applying the method of M. J. D. Powell to the experimental data.

Glossary

f_i	fugacity of component i
H	Henry's constant
j_{ij}	binary interaction parameter
k_{ij}	binary interaction parameter
K_i	y_i/x_i
P	total pressure
P_i°	vapor pressure of component i
T	temperature

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Gas–Liquid Equilibrium in Mixtures of Hydrogen and Quinoline

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Gas–liquid equilibrium in hydrogen/quinoline mixtures was experimentally determined at four temperatures from 190 to 430 °C and seven pressures from 20 to 250 atm in a flow apparatus. Vapor pressure of quinoline was measured in the same apparatus. The new mixture equilibrium data are compared with general correlations that have been developed for hydrogen/hydrocarbon mixtures.

Introduction

The solubility of a light supercritical component in a heavy liquid is of both theoretical and practical interest. The theoretical interest reflects the basic nature of the solubility problem as an intermolecular force phenomenon. The practical interest stems from engineering design needs. With the recent intensified development of hydrotreating processes particularly coal liquefaction, equilibrium data of hydrogen/oil mixtures are in demand. Previous studies of phase equilibrium of hydrogen/solvent systems were mostly confined to relatively low temperatures. The literature was reviewed by Simnick et al. (*8*) and updated in ref 10. Work in this laboratory has produced data at conditions of elevated temperatures (to 430 °C) and pressures (to 250 atm). The systems studied so far include the binary mixtures of hydrogen with tetralin (*8*), bicyclohexyl (*7*), diphenylmethane (*9*), 1-methylnaphthalene (*11*), *m*-cresol, and *m*-xylene (*10*). In this work we investigate mixtures of hydrogen and a hetroatom-containing hydrocarbon. Solvents of this type have not been studied with respect to hydrogen solubility at high pressures.

The experimental apparatus and procedure of this study have been described, and the attainment of equilibrium in the apparatus at the operation conditions has been established (*8*–*11*). The same apparatus description and equilibrium consideration apply to this work and therefore will not be reiterated.

Materials

The hydrogen gas used in this work was supplied by Air Products Co. with a reported minimum purity of 99.95%. The quinoline purchased from Fisher Scientific Co. as certified reagent grade of 99+% purity showed a deep purple indicating presence of the air oxidation product, quinoline *N*-oxide. It was therefore purified by fractional distillation over zinc dust at reduced pressure under a helium blanket. The distillate was colorless and was stored over anhydrous sodium sulfate prior to use.

Quinoline from both the gas and liquid streams from the equilibrium cell was checked for possible chemical reactions with a gas chromatograph equipped with a thermal conductivity detector. The analysis indicated a small amount of impurities in the sample from the gas stream. However, the sum of the peak areas of these impurities never amounted to more than 1.5% of the total peak areas of the sample. The most probable impurity is isoquinoline. Quinoline from the cell effluents did show a slight coloration. Therefore, all quinoline collected from the cell effluents was distilled before reuse. The distillation yielded a colorless overhead product which was reused. A small amount of colored residue was left in the still and was discarded.

The rate of thermal decomposition of quinoline was studied by Johns and co-workers (*3*) who reported an observed rate

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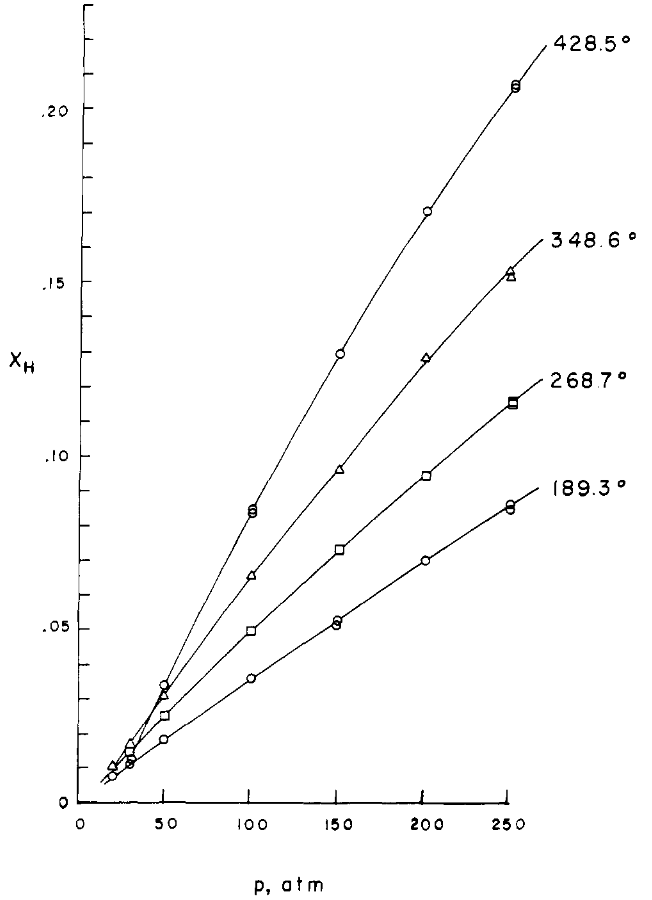

Figure 1. Solubility of hydrogen in quinoline.

of 1 mol %/h at 510-535 °C.

Results and Discussion

Figure 1 shows the solubility isotherms of hydrogen in quinoline at four temperatures from 189.3 to 428.5 °C. At each temperature observations were made at seven pressures from 20 to 250 atm. However, the data at 20 atm and 428.5 °C were not measured due to the excessively high degree of vaporization of quinoline. The equilibrium vapor compositions are shown in Figure 2. At least two samples were taken at a fixed temperature and pressure and are shown in the figure as a doublet, where possible. A single point shown in the figures represents indistinguishable multiple samples. In general the multiple samples do not deviate by more than 1% in mole fraction composition of hydrogen.

The averaged values of the equilibrium saturated gas and liquid compositions are reported in Table I. Vapor pressure of quinoline is given as the first entry at each temperature. The subatmospheric value at 189.3 °C was obtained from the literature (*4*). The values at other temperatures were interpolated from the experimental data of this work. The *K* values of hydrogen and quinoline, calculated from the averaged experimental data of y_H and x_H, are also contained in Table I and respectively shown in Figures 3 and 4.

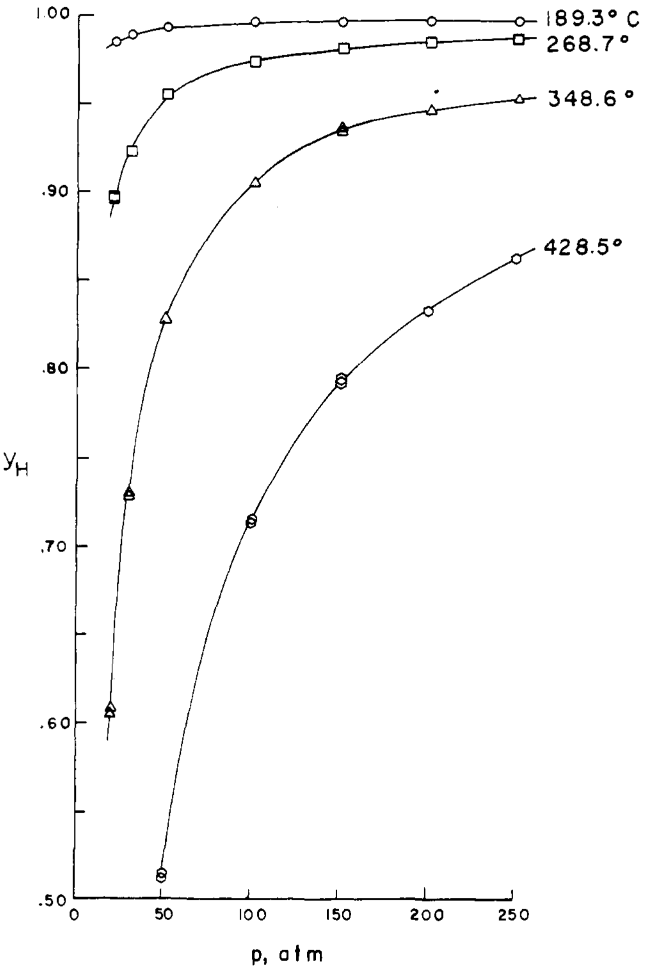

Figure 2. Mole fraction of hydrogen in saturated gas in H_2/quinoline mixtures.

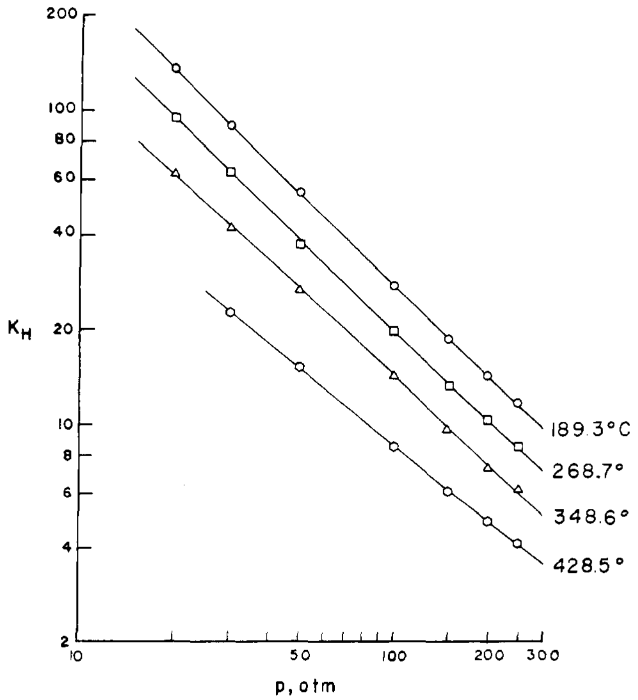

Figure 3. Vaporization equilibrium ratio of hydrogen in H_2/quinoline.

A useful application of the data is to test the accuracy of general correlations. Figures 5 and 6 show the comparisons of the present data with the correlations of Chao-Seader (*1*) and Grayson-Streed (*2*) that are in industrial use. The values of physical properties required in the correlations are presented in Table II for quinoline. Chao and Seader reported the needed values for hydrogen. The critical temperature and pressure of quinoline are available from Riddick and Bunger (*6*). Lydersen's method (*5*) was applied to estimate the critical volume. The

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

P, atm	x_H	y_H	K_H	K_Q
		189.3 °C		
0.3115[a]	0	0		
19.88	0.0072	0.9845	136.7	0.0156
30.06	0.0110	0.9893	89.9	0.0108
49.99	0.0180	0.9930	55.2	0.00713
100.0	0.0359	0.9963	27.75	0.00384
150.4	0.0527	0.9972	18.92	0.00296
200.0	0.0700	0.9977	14.25	0.00247
249.7	0.0857	0.9978	11.64	0.00241
		268.7 °C		
1.918[a]	0	0		
20.00	0.0095	0.8959	94.3	0.1051
29.99	0.0147	0.9277	63.1	0.0734
50.06	0.0252	0.9558	37.9	0.0453
99.67	0.0495	0.9757	19.71	0.0256
150.4	0.0730	0.9821	13.45	0.01931
200.0	0.0946	0.9861	10.42	0.01535
249.7	0.1160	0.9878	8.52	0.01380
		348.6 °C		
7.300[a]	0	0		
20.05	0.0097	0.6029	62.3	0.401
30.12	0.0169	0.7282	43.1	0.276
49.99	0.0308	0.8278	26.9	0.1777
100.4	0.0652	0.9040	13.87	0.1027
149.7	0.0965	0.9345	9.68	0.0725
199.3	0.1290	0.9465	7.34	0.0614
249.7	0.1532	0.9539	6.23	0.0544
		428.5 °C		
19.55[a]	0	0		
30.26	0.0118	0.2607	22.1	0.748
49.99	0.0332	0.5107	15.38	0.506
100.7	0.0837	0.7143	8.53	0.312
149.3	0.1294	0.7939	6.14	0.237
199.0	0.1708	0.8333	4.88	0.201
249.4	0.2071	0.8634	4.17	0.1723

[a] Vapor pressure of quinoline.

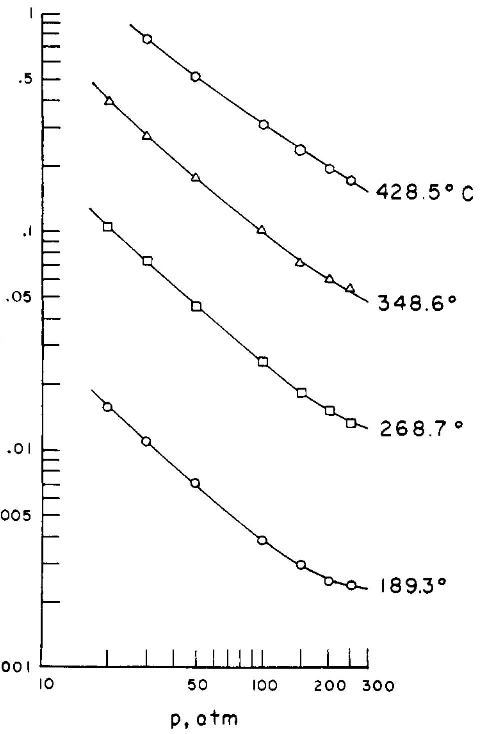

Figure 4. Vaporization equilibrium ratio of quinoline.

value of the acentric factor was obtained from the vapor pressure data at T_r = 0.7 according to the definition by Pitzer.

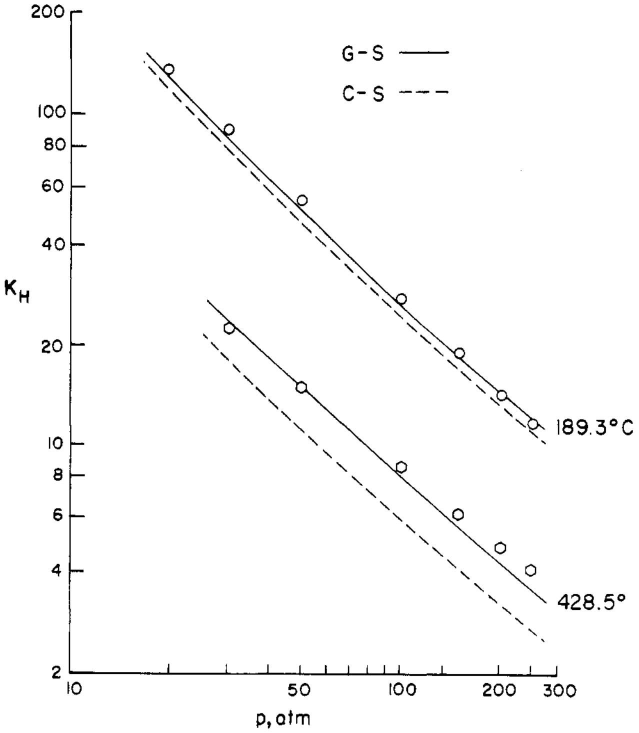

Figure 5. Comparison of K values of hydrogen with correlations.

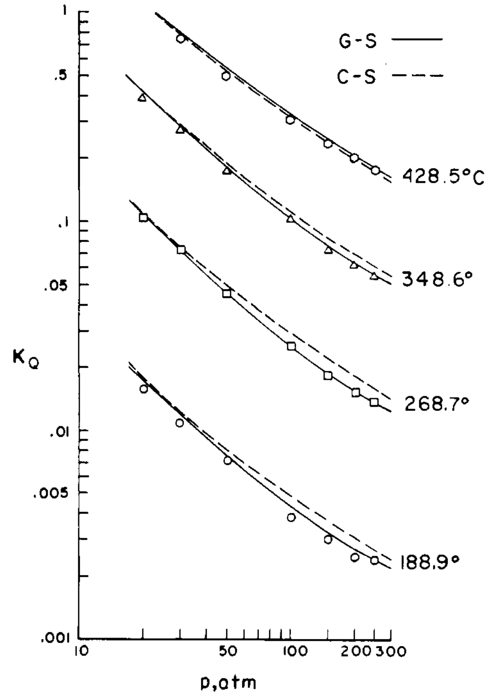

Figure 6. Comparison of K values of quinoline with correlations.

Table II. Physical Properties of Quinoline

T_C	794.5 K
P_C	57 atm
V_C	403 mL/(g-mol)
ω	0.320
δ	10.9 (cal/mL)$^{1/2}$
V (25 °C)	140.7 mL/(g-mol)

The solubility parameter was calculated from the literature value of heats of vaporization (*6*).

The comparisons show that the K values of hydrogen from the Chao-Seader correlation appear consistently low, while the Grayson-Streed correlation provides a better representation of the data with a maximum deviation of about 15%. The better representation by the Grayson–Streed correlation is expected since the Chao–Seader correlation for hydrogen was limited by its data base to temperatures below 260 °C. Grayson and Streed extended the temperature range by using experimental data of their own at temperatures up to 480 °C. Chao–Seader predicted the K values of quinoline in fair agreement with experimental data, but the deviations are up to about 25% at the higher pressures of the lower isotherms. The Grayson–Streed correlation appears to well represent the K values of quinoline up to the highest pressure studied. Both correlations are extrapolated with respect to solubility parameter value to apply to the present system. The result indicates that improvement of the Chao–Seader type correlations to apply to heteroatom-containing hydrocarbons is possible. This conclusion is supported by previous studies in this laboratory (*7–11*).

Glossary

K	vaporization equilibrium ratio, y/x
p	pressure, atm
T	temperature, K
T_r	reduced temperature, T/T_c
$\tilde{V}$	molar volume, mL/g-mol
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the gas phase
δ	solubility parameter, $(cal/mL)^{1/2}$
ω	acentric factor

Subscripts

C	critical properties
H	hydrogen
Q	quinoline

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Standard Electromotive Forces of the Cell $Pt;H_{2(1\ atm)},HCl_{(m)},AgCl;Ag$ Containing Mixtures of Dimethyl Sulfoxide and Water between +25 and −12 °C

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Measured emf's for the cell $Pt;H_{2(g,1\ atm)},HCl,AgCl;Ag$ and derivation of the standard cell potentials are tabulated for water at 25 and 0 °C, for 20% (w/w) Me_2SO–H_2O at +25, 0, and −5.5 °C, and for 30% (w/w) Me_2SO–H_2O at +25, 0, and −12 °C. The determination of standard molal emf's of the hydrogen–silver, silver chloride electrochemical cell containing mixtures of dimethyl sulfoxide (Me_2SO) and water at low temperatures is needed for reliable pH measurements in mixed solvents at normal and subzero temperatures.

Introduction

Reliable pH measurements in mixed solvents are needed at low temperatures, since pH changes may contribute to the injury of biological systems during cooling and freezing (*7*, *31*, *32*). Solutions used for the low-temperature preservation of cells, tissues, and organs usually incorporate a binary mixed solvent due to the addition of a nonelectrolyte compound such as dimethyl sulfoxide (Me_2SO) or glycerol (*25*, *28*). These compounds, often called cryoprotectants, act colligatively to depress the freezing point of the medium and also to reduce the amount of ice at any temperature during freezing. This is thought to be the principal mechanism of cryoprotection (*24*).

Investigations into the factors affecting the low-temperature preservation of smooth muscle tissue (*7*, *31*, *32*) showed that its functional recovery after low-temperature storage in unfrozen media containing Me_2SO is dependent upon the initial pH of the bathing solution. However, in these and other studies emphasizing pH changes as an important factor for the survival of biological systems after exposure to low temperatures, all measurements of hydrogen ion activity were carried out at ambient temperatures with a glass/calomel cell standardized against aqueous buffers. These measurements were subject to errors of unknown magnitude on account of the indeterminable asymmetry potential of the glass membrane and the liquid junction potentials within the cell, and as a result the true pH of the tissue and its bathing medium remained uncertain.

Solvent composition and temperature can have a marked effect upon the value and measurement of the hydrogen ion activity of a solution (*2*, *6*, *26*) and although Khoo (*20*, *21*) has measured the standard electromotive forces of hydrogen–silver halide cells containing mixtures of Me_2SO and water at 25 °C, little work has been done to establish pH scales in aqueous mixed solvents at low temperatures.

The pH-dependent recovery of smooth muscles from storage at −13 °C in unfrozen solutions containing 30% Me_2SO (*31*, *32*) has defined one set of conditions under which reliable electrochemical measurements of hydrogen ion activity would be useful. This paper describes the determination of standard molal emf's in mixtures of dimethyl sulfoxide and water at temperatures between +25 and −12 °C, thereby providing a basis for the application of the hydrogen–silver, silver chloride

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