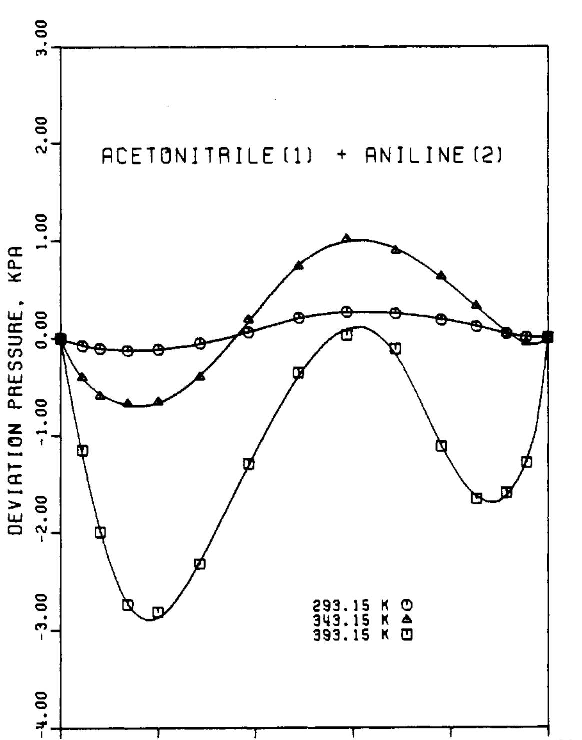

Figure 5. Deviation from Raoult's law for the acetonitrile (1) + aniline (2) system at 293.15, 343.15, and 393.15 K.

increased, the tendency was toward larger negative deviation in the region of high acetone concentration and larger positive deviation in the region of low acetone concentration. The activity coefficients for this system are shown in Figure 4. Note that γ_2^∞ goes through a minimum with respect to temperature.

Perhaps the most unusual system, on the basis of the shape of the P_D vs. x_1 curve, is acetonitrile + aniline (see Figure 5). The curves cross the Raoult law line ($P_D = 0$) at two places for all three temperatures and will apparently show only negative deviation just above the range of temperatures measured. The activity coefficients, shown in Figure 6, all cross over the $\gamma = 1.0$ line except for the γ_1 curve at 393.15 K, which appears to be "unfolding" and turning upward to form a more regularly shaped γ curve.

Glossary

B	second virial coefficient, cm^3 mol^{-1}
G	Gibbs function, J mol^{-1}
P	pressure, kPa

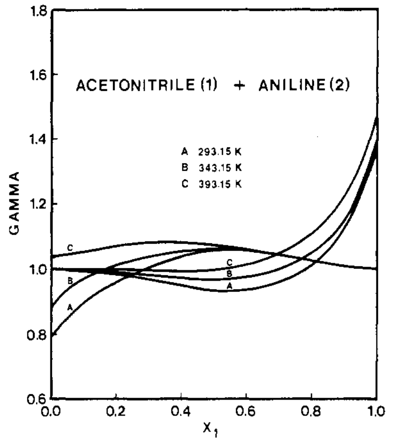

Figure 6. Activity coefficients for the acetonitrile (1) + aniline (2) system at 293.15, 343.15, and 393.15 K.

R	gas constant
T	absolute temperature, K
V	molar volume, cm^3 mol^{-1}
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient

Subscripts

1	more volatile component
2	less volatile component

Superscripts

E	excess property
L	liquid-phase property
V	vapor-phase property
^	mixture component property
′	vapor pressure

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Gas–Liquid Equilibrium in the Hydrogen + *n*-Decane System at Elevated Temperatures and Pressures

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Vapor–liquid equilibrium data for mixtures of hydrogen and *n*-decane are reported at four temperatures (189.3, 230.2, 269.8, 310.3 °C) and at pressures from 20 to 250 atm.

Introduction

There recently has been an increased interest in gas–liquid equilibrium data for mixtures of hydrogen and organic liquids due

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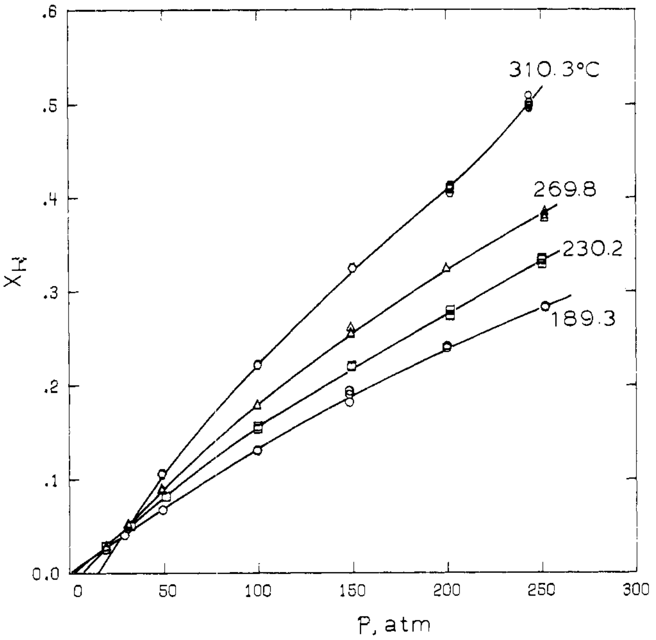

Figure 1. Solubility of hydrogen in *n*-decane.

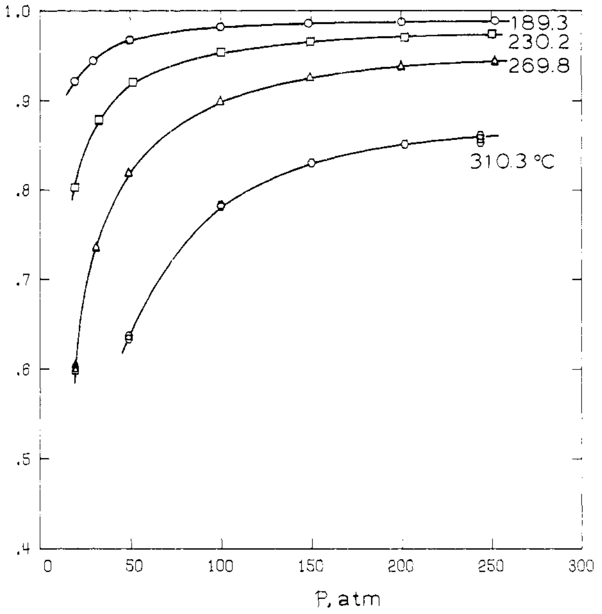

Figure 2. Mole fraction of hydrogen in saturated vapor in H_2 + *n*-decane.

to the intensified development of hydrotreating processes, especially in the area of coal conversion. Previous data in the literature have been reviewed by Simnick et al. (*1*, *3*). Most of the available data were at temperatures below 200 °C. In this work we report gas-liquid equilibrium data in mixtures of hydrogen and *n*-decane at temperatures between 190 and 310 °C and pressures between 20 and 250 atm. No fluid-phase equilibrium data have been reported previously for this mixture system.

Experimental Section

The apparatus and procedure used in this study have been described previously by Simnick et al. (*1*). A minor change has been made in the apparatus with the addition of a Heise gauge (Model CMM) which measures pressures below 34 atm to an increased accuracy of ±0.03 atm.

Table I. Gas-Liquid Equilibrium Data for Hydrogen + *n*-Decane

p, atm	x_H	y_H	K_H	K_D
		189.3 °C		
1.4477[a]				
19.01	0.0251	0.9216	36.71	0.0804
29.15	0.0408	0.9446	23.15	0.0578
49.4	0.0678	0.9676	14.26	0.0348
99.6	0.1309	0.9823	7.504	0.0204
148.3	0.1890	0.9860	5.217	0.0173
200.0	0.2406	0.9877	4.105	0.0162
251.9	0.2832	0.9891	3.492	0.0152
		230.2 °C		
3.485[a]				
19.16	0.0289	0.8021	27.75	0.2038
32.46	0.0511	0.8786	17.19	0.1279
51.1	0.0818	0.9207	11.26	0.0864
99.9	0.1550	0.9539	6.154	0.0545
149.5	0.2202	0.9657	4.385	0.0440
201.7	0.2760	0.9706	3.517	0.0406
250.4	0.3324	0.9740	2.930	0.0389
		269.8 °C		
7.132[a]				
19.35	0.0286	0.6025	21.07	0.4092
30.92	0.0533	0.7367	13.82	0.2781
48.8	0.0903	0.8198	9.079	0.1981
99.5	0.1799	0.9001	5.003	0.1218
149.2	0.2582	0.9266	3.589	0.0989
199.7	0.3249	0.9391	2.891	0.0902
251.8	0.3825	0.9446	2.470	0.0897
		310.3 °C		
13.378[a]				
49.9	0.1059	0.6355	5.998	0.4077
99.7	0.2220	0.7825	3.525	0.2796
150.1	0.3247	0.8303	2.557	0.2513
201.7	0.4098	0.8505	2.075	0.2533
243.7	0.5013	0.8581	1.712	0.2845

[a] Vapor pressure of *n*-decane (*4*).

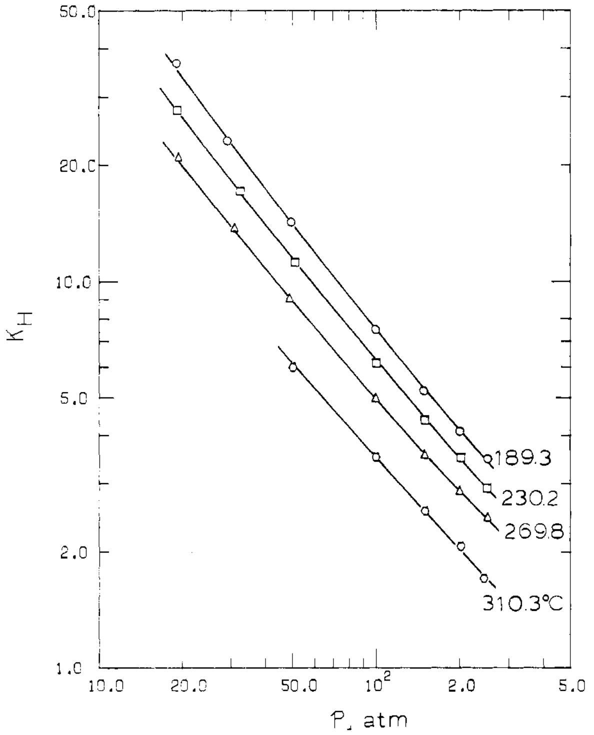

Figure 3. Vaporization equilibrium ratio of hydrogen in H_2 + *n*-decane.

A flow apparatus was used to minimize thermal decomposition of the *n*-decane in the high-temperature zone. The attainment of equilibrium in this flow apparatus has been verified in careful studies described in previous reports from this laboratory (*1*–*3*).

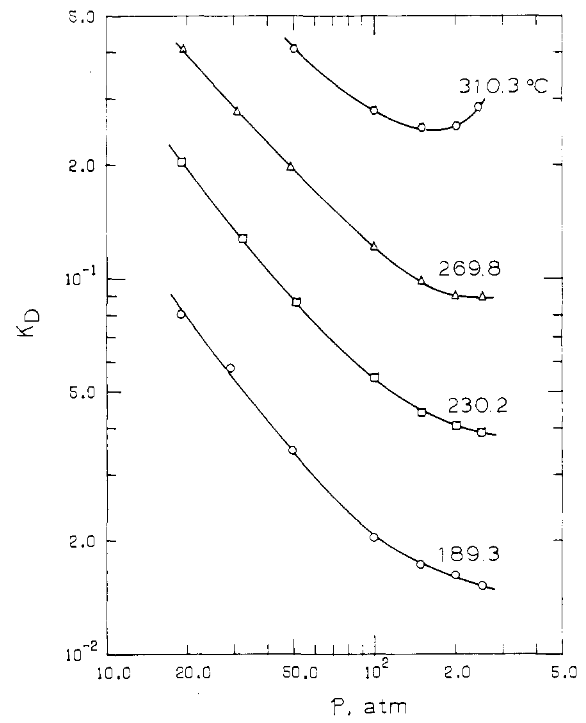

Figure 4. Vaporization equilibrium ratio of *n*-decane in H_2 + *n*-decane.

Hydrogen gas was supplied by Airco with a purity of 99.95%. Gold label grade *n*-decane was purchased from the Aldrich Chemical Co. with a reported purity of 99+%.

Samples of the condensates from both the overhead and bottom cell effluents were collected at each experimental condition. The condensates were analyzed on a Chicago Nuclear gas chromatograph and no decomposition products were found at any of the conditions studied. Nevertheless, *n*-decane recovered from the cell effluents was fractionally distilled under a reduced nitrogen atmosphere before being reused.

The fluctuation of the equilibrium cell temperatures was less than 0.2 °C during the measurement of all of the points on an isotherm.

Results

Figure 1 shows the mole fraction of hydrogen in the liquid phase at four temperatures between 189 and 310 °C. Data were taken at seven pressures between 20 and 250 atm at each temperature except for the highest temperature, 310 °C, where data were taken at only five pressures from 50 to 250 atm. Excessive vaporization of *n*-decane at the lower pressures and highest temperature made it impossible to take accurate data. The isothermal solubilities extrapolate smoothly to $x_H = 0$ at the vapor pressure of *n*-decane. The vapor pressure of *n*-decane is taken from ref 4. The saturated vapor compositions are shown in Figure 2. At each set of temperature and pressure conditions at least two samples of both the overhead and bottoms were taken. The agreement among replicate points was, in general, within 1% in mole fraction of hydrogen. The individual data points are shown in Figures 1 and 2 when they can be distinguished. The average values of the replicate samples are reported in Table I. These average values of x_H and y_H were used to calculate the equilibrium ratios which are also reported in Table I and shown respectively in Figures 3 and 4 for hydrogen and *n*-decane.

Glossary

K	vaporization equilibrium ratio, $K = y/x$
p	pressure, atm
t	temperature, °C
x	mole fraction in the liquid phase
y	mole fraction in the gas phase

Subscripts

D	*n*-decane
H	hydrogen

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Excess Enthalpies for Mixtures of Acetonitrile and Aromatic Hydrocarbons

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Measurements of excess enthalpies were carried out at 25 and 41.2 °C for binary mixtures of acetonitrile with benzene, toluene, ethylbenzene, *p*-xylene, and *m*-xylene.

This paper is part of an experimental investigation of the thermodynamic excess functions of binary mixtures consisting of an aromatic hydrocarbon and acetonitrile. This paper reports excess enthalpies for these systems.

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