data more accurately, and the use of the second and higher order Auslander equations is recommended for representing the physical properties of mixtures.

Glossary

A_{21}, B_{12}, B_{21}	constants in eq 6
A–E	constants in eq 7
G^*	molar Gibbs free energy of activation for viscous flow
h	Plank constant
M	molecular weight
N	Avogadro number
R	gas constant
T	absolute temperature
x	mole fraction
ν	kinematic viscosity
ν_{12}, ν_{21}, etc.	fitting constants in eq 3–5

Subscripts

1,2　　　　components 1 and 2

Superscripts

E　　　　excess property

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Gas–Liquid Equilibrium in Hydrogen + n-Hexadecane and Methane + n-Hexadecane at Elevated Temperatures and Pressures

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Experimental results are presented for gas–liquid phase equilibria in binary mixtures of n-hexadecane with hydrogen at four temperatures from 190 to 391 °C and with methane from 190 to 430 °C. At each temperature, measurements were made at pressures from 20 to 250 atm or to near the critical pressure of the mixtures.

Introduction

This work is part of a continuing study of phase equilibrium in mixtures of light gases and heavy hydrocarbon liquids at elevated temperatures and pressures. In the past, attention was specifically aimed at polynuclear aromatic and naphthenic hydrocarbons such as tetralin (*3*), methylnaphthalene (*6*), diphenylmethane (*4*), and bicyclohexyl (*2*).

In this work we study mixtures of a long chain paraffin with hydrogen and with methane. Measurements were made at temperatures from 190 to 390 °C and pressures from 20 to 250 atm for hydrogen + n-hexadecane. No literature data are available for these mixtures at conditions comparable to this study. For the methane + n-hexadecane system, the temperatures studied were in the range 190–430 °C and pressures were from 20 atm to approaching the critical pressure of the mixtures. Sultanov and co-workers (*5*) reported experimental results for this system at temperatures from 100 to 350 °C up to the critical pressures of the mixtures. Low-pressure solubility data of methane in n-hexadecane were determined by Chappelow and Prausnitz (*1*) in the temperature range 25–200 °C.

Experimental Section

The same apparatus and procedures described by Simnick et al. (*3*) were used in this work.

Hydrogen gas was supplied by Airco with a minimum purity of 99.95%. Methane was obtained from Matheson and n-

hexadecane from Matheson Coleman and Bell Co.; the purities of both chemicals are claimed to be 99+%. The thermal stability of n-hexadecane was checked by gas chromatography during all of the experiments. No more than 1% of impurities was detected in the n-hexadecane from the cell effluents at any conditions studied.

Fluctuations in the temperature of the equilibrium cell during the course of all the measurements on an isotherm were within 0.1 °C.

The attainment of equilibrium in the flow apparatus used was verified by varying the liquid feed flow rate. Tests were made at 100 atm and 390.9 °C with mixtures of hydrogen + n-hexadecane and at several pressures at 189.3 °C with mixtures of methane + n-hexadecane. No appreciable variations of the phase compositions were observed as the flow rate was varied.

Results and Discussion

Figure 1 shows the solubility of hydrogen in n-hexadecane at four temperatures from 188.5 to 390.9 °C as a function of pressure, while Figure 2 shows the saturated equilibrium compositions of the vapor phase for the same mixtures. At each condition of temperature and pressure, at least two samples of both the overhead and bottom cell effluents were taken, and the agreement among replicate samples was within 1% in mole fraction of hydrogen. The individual data points are shown in the figures when they can be differentiated. The average values of the replicate samples are given in Table I. The vapor compositions at 188.5 °C are practically all hydrogen, and equilibrium ratios of n-hexadecane at this isotherm are extremely sensitive to the last few digits in the value of y_H. The values of y_H are, therefore, reported in the table to five digits.

The experimental results for methane + n-hexadecane are shown in Figures 3 and 4. At 189.3 °C, the pressures were measured up to 250 atm. For the three higher isotherms,
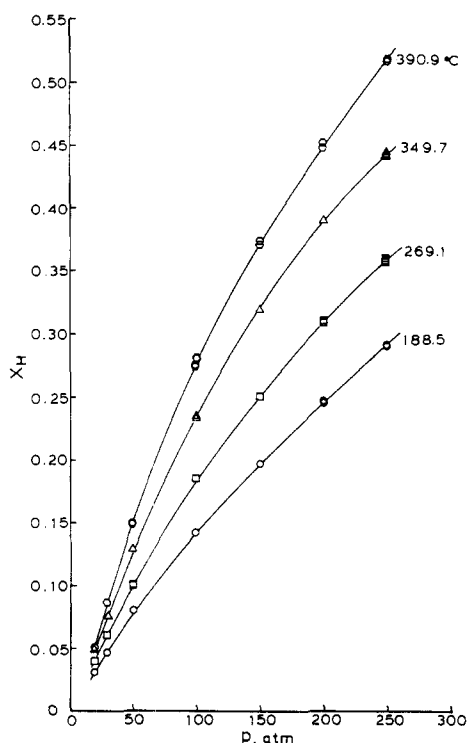
Figure 1. Solubility of hydrogen in liquid n-hexadecane.

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

Table I. Vapor-Liquid Equilibrium Data for Hydrogen + n-Hexadecane

p, atm	x_H	y_H	K_H	K_{HD}
		188.5 °C		
20.05	0.0311	0.996 66	32.05	0.003 45
29.90	0.0468	0.997 82	21.32	0.002 29
50.0	0.0757	0.998 50	13.19	0.001 623
101.7	0.1428	0.999 09	7.00	0.001 062
149.5	0.1978	0.999 29	5.05	0.000 885
199.5	0.2468	0.999 39	4.05	0.000 810
249.4	0.2928	0.999 45	3.41	0.000 778
		269.1 °C		
19.83	0.0407	0.964 8	23.71	0.036 7
30.24	0.0617	0.975 9	15.82	0.025 7
50.7	0.1007	0.984 9	9.78	0.016 79
101.8	0.1854	0.991 87	5.35	0.009 98
149.7	0.2515	0.993 62	3.95	0.008 52
199.7	0.3104	0.994 50	3.20	0.007 98
248.9	0.3597	0.995 03	2.77	0.007 76
		349.7 °C		
19.97	0.0497	0.808 3	16.26	0.202
29.92	0.0764	0.866 3	11.34	0.144 8
50.4	0.1293	0.917 9	7.10	0.094 3
100.1	0.2354	0.955 3	4.06	0.058 5
150.9	0.3201	0.966 5	3.02	0.049 3
200.7	0.3903	0.971 3	2.49	0.047 1
249.3	0.4458	0.975 7	2.19	0.043 8
		390.9 °C		
19.69	0.0513	0.605 4	11.80	0.416
30.02	0.0857	0.720 5	8.41	0.306
50.2	0.1488	0.822 4	5.53	0.209
100.7	0.2782	0.897 7	3.23	0.141 7
100.4	0.2759	0.898 8	3.26	0.139 8
150.4	0.3724	0.927 1	2.49	0.116 2
199.9	0.4511	0.937 8	2.08	0.113 3
250.5	0.5192	0.945 2	1.82	0.114 0

Figure 3. Solubility of methane in liquid n-hexadecane.

measurements were made up to near the critical pressure of the mixtures at each temperature.

The experimental results of this work are summarized in Table II. Also shown in Figures 3 and 4 are data of Sultanov and
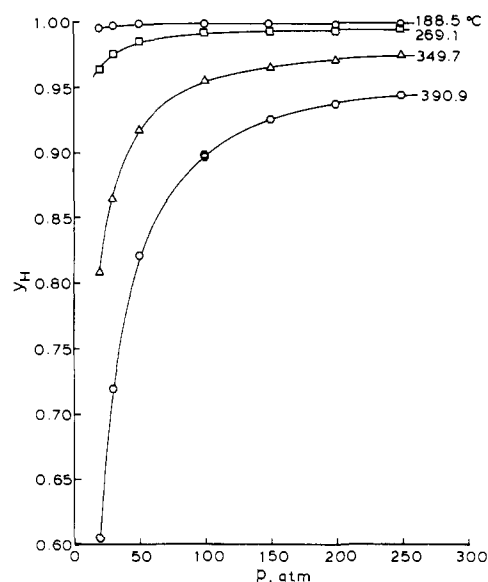
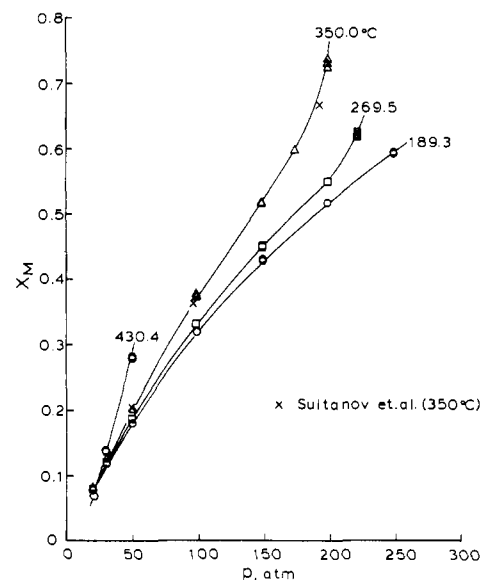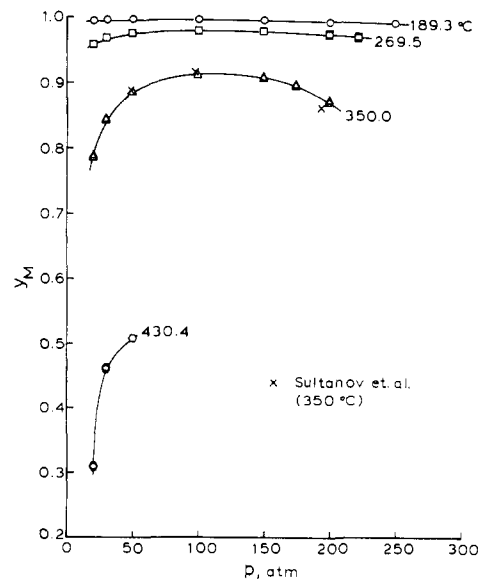**Figure 4.** Mole fraction of methane in saturated vapor in methane + n-hexadecane.

Table II. Vapor–Liquid Equilibrium Data for
Methane + n-Hexadecane

p, atm	x_M	y_M	K_M	K_{HD}
		189.3 °C		
20.02	0.0801	0.995 44	12.43	0.004 96
30.71	0.1187	0.996 58	8.40	0.003 88
49.8	0.1824	0.997 22	5.47	0.003 40
100.0	0.3207	0.997 18	3.11	0.004 15
149.9	0.4326	0.996 36	2.30	0.006 42
200.9	0.5193	0.994 67	1.92	0.011 09
249.3	0.5958	0.992 06	1.67	0.019 64
		269.5 °C		
20.50	0.0831	0.958 0	11.53	0.045 8
30.23	0.1208	0.968 7	8.02	0.035 6
50.0	0.1884	0.976 5	5.18	0.029 0
99.5	0.3322	0.980 8	2.95	0.028 8
149.9	0.4539	0.979 8	2.16	0.037 0
200.6	0.5512	0.975 4	1.77	0.054 8
222.5	0.6229	0.971 9	1.56	0.074 5
		350.0 °C		
20.71	0.0836	0.793 0	9.49	0.226
31.39	0.1265	0.845 3	6.68	0.177 1
50.0	0.2032	0.886 5	4.36	0.142 4
99.7	0.3716	0.913 2	2.46	0.138 1
150.3	0.5178	0.909 7	1.76	0.187 3
176.1	0.5968	0.897 0	1.50	0.256
201.3	0.7371	0.873 3	1.18	0.482
		430.4 °C		
20.87	0.0697	0.309 7	4.44	0.742
30.77	0.1363	0.463 2	3.40	0.622
49.8	0.2822	0.509 9	1.81	0.683

co-workers at 350 °C. This is the highest temperature reported by Sultanov et al. and is the only temperature at which their study and ours coincide. The data shown in Figure 4 are read from their graph. The agreement with our data seems reasonable.

Glossary

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

Subscripts

H	hydrogen
HD	n-hexadecane
M	methane

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Excess Thermodynamic Functions for Ternary Systems. 6. Total-Pressure Data and G^E for Acetone–Ethanol–Water at 50 °C

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Isothermal P–x data for the ternary system acetone–ethanol–water at 50 °C are reported, together with data for the constituent binaries. Data reduction by Barker's method provides a correlation for G^E.

The VLE measurements reported here are for the acetone (1)–ethanol (2)–water (3) system at 50 °C. Experimental values of total vapor pressure are presented for the full composition range of the three constituent binaries and for six runs on ternary mixtures formed by additions of each pure species to mixtures of the other two in molar proportions of approximately 2 to 1. The apparatus is that of Gibbs and Van Ness (8) as modified by DiElsi et al. (7).

The acetone was chromatoquality reagent from Matheson Coleman and Bell; the reagent-grade ethanol was supplied by U.S. Industrial Chemicals, and the water was doubly deionized. Except for being degassed, all reagents were used as received, with indicated purities of at least 99.8 mol %. Vapor pressures of the pure constituents measured in this work and comparable

Table I. Vapor Pressures of Pure Species at 50 °C in kPa

	acetone (1)	ethanol (2)	water (3)
present work	82.029	29.484	12.355
	82.029	29.515	12.375
	82.015	29.490	12.331
	82.000	29.493	12.358
av value	82.018	29.496	12.355
lit. values	81.989 (7)	29.494 (4)	12.345 (3, 11)
	81.835 (6)	29.481 (11)	12.350 (12)
		29.493 (12)	12.347 (5)
		29.472 (5)	12.349 (10)

values from the literature are reported in Table I. The P_i^{sat} values in all calculations are fixed at averages of our experimental measurements.

Results and Correlations

Tables II–IV give experimental values of total pressures for the three constituent binaries, and Table V contains all data for