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Vapor–Liquid Equilibria of Hydrogen–2,2,4-Trimethylpentane and Hydrogen–Toluene Systems at High Pressures and Temperatures

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A static method for measuring high-pressure high-temperature vapor–liquid equilibria, described in a previous article, has been extended to hydrogen–hydrocarbon systems. The validity of the experimental technique is tested on known systems. Excellent agreement with literature values is obtained. New data are presented for the systems hydrogen–2,2,4-trimethylpentane at 250 °C between 30 × 10^5 and 208 × 10^5 Pa and hydrogen–toluene at 295 °C between 64 × 10^5 and 308 × 10^5 Pa.

Introduction

Knowledge of hydrogen solubility in hydrocarbons is important to the petrochemical industry (hydrotreatment). Until recently, few workers were concerned with high-temperature measurements. Recently, Simnick et al. (*1*) developed a flow apparatus from which hydrogen solubility data were obtained. In this paper we report data using a static apparatus described earlier (*2*) which enables experiments to be done up to 4 × 10^7 Pa and 400 °C. A special feature of this apparatus is the ability to measure vapor–liquid equilibria near the critical point.

Experimental Section

Apparatus. The apparatus described earlier (*2*) has the unique feature of sampling both the liquid and vapor phases which are in equilibrium. The method consists of drawing a sample from the liquid phase and vapor phase by means of a valve. When the valve is opened for a very short time (10^{-2} s) a small sample (about 1 μL) of each phase is automatically injected from the 50-cm^3 cell into a chromatographic circuit. The mixture is stirred by means of a small magnet driven from the outside of the cell by a series of solenoids.

The temperature is maintained to within 0.2 °C and measured with an accuracy of 0.5 °C. Maximum temperature is about 400 °C.

The total pressure is measured with a pressure transducer (Kaman) calibrated against a dead-weight balance (Budenberg Model 280 H). Accuracy in pressure is about 40 KPa over the whole pressure range.

Phase Analysis. Gas–liquid chromatography is the method which is best suited for hydrogen–hydrocarbon concentrations. Of the different types of detectors such as photoionization, flame ionization, electron capture, and thermal conductivity, only the last one may be used to analyze hydrogen–hydrocarbon mixtures. Selective sensitivity with a thermal conductivity detector depends on carrier gas nature.

In order to maximize the sensitivity for both hydrogen and hydrocarbon, we use neon as the carrier gas. Hydrogen has the highest thermal conductivity coefficient while hydrocarbon thermal conductivity coefficients are usually small. Neon has an intermediate coefficient. In order to properly use the detectors, and integrator, it is necessary to change the polarity of electrical signal between hydrogen and hydrocarbon measurement.

Table I. Density and Refractive Index of Liquid Components

	hydrocarbon	this work	lit. values
refractive index at 20.0 °C	toluene	1.4969_1	1.4970[a]
			1.4969[b]
	isooctane	1.39142	1.39142[a]
density at 20.0 °C	toluene	0.86698	0.86696[a]
	isooctane	0.69188	0.69192[a]

[a] Timmermans, J.; "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, Amsterdam, 1965. [b] *Beilstein, 4th ed.*, 1 (1918); 5 (1922).

Table II. Vapor–Liquid Equilibrium Data for the System Hydrogen (1)–2,2,4-Trimethylpentane (2)

T, °C	$10^{-5}P$, Pa	x_1	y_1	k_1	k_2
226.0	30		0.445	11.12	0.578
226.0	62	0.110	0.676	6.15	0.364
226.0	119	0.217	0.780	3.59	0.281
226.0	180	0.312	0.829	2.66	0.249
226.0	246		0.847	2.03	0.262
226.0	248	0.421		2.01	0.264
226.0	314	0.499	0.849	1.70	0.301
226.0	368	0.580		1.42	0.417
250.0[a]	31.5	0.039		6.33	0.784
250.0	80.0	0.171		3.70	0.443
250.0	102.0	0.232		2.91	0.424
250.0	130.0		0.704	2.46	0.415
250.0	150.5	0.345		2.05	0.447
250.0	160.5	0.373		1.89	0.470
250.0	170.5	0.402		1.74	0.502
250.0	174.0		0.697	1.70	0.514
250.0	181.0	0.428		1.62	0.538
250.0	197.5	0.467		1.42	0.630
250.0	200.0		0.651	1.36	0.671
250.0	204.0	0.496	0.636	1.28	0.722
250.0		0.524	0.550	1.05	0.945
250.0[b]	49.0		0.473	5.43	0.577
250.0	50.5	0.093		5.16	0.573
250.0	78.0		0.623	3.73	0.453
250.0	104.0		0.670	2.82	0.433
250.0	144.0	0.335	0.708	2.11	0.439
250.0	187.0	0.444		1.54	0.568

[a] First experiment. [b] Second experiment.

Under good conditions, a quantitative GLC analysis shows hydrogen mole fraction determinations have error less than 0.009 in liquid and 0.012 in vapor phase.

Chemicals. The hydrogen was supplied by L'Air Liquide, which is pure to better than 99.95%. 2,2,4-Trimethylpentane and toluene were obtained from Fluka and Merck, respectively. These two components have a guaranteed purity of not less than 99.50% and have been used without further purification.

No impurity could be detected by chromatography and the results of refractive index and density given in Table I confirm high purity of toluene and isooctane.

Results and Discussion

Hydrogen–2,2,4-Trimethylpentane. This system has been previously studied with a static apparatus by Peter and Reinhartz (*3*) at three temperatures, namely, 150.8, 198.5, and 226.2 °C.

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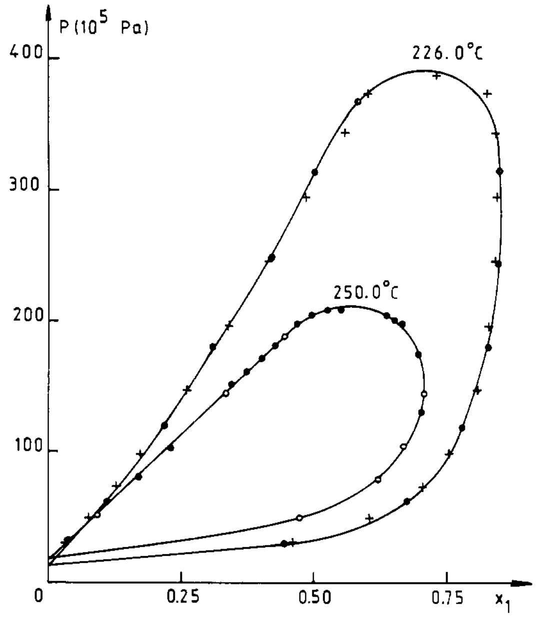

Figure 1. Vapor-liquid equilibrium data for the system hydrogen-2,2,4-trimethylpentane at 226.0 and 250.0 °C: (+) 226.2 °C isotherm (ref 3); (⊙) 226.0 °C isotherm (present work); (○) 250.0 °C isotherm, first experiment of this work; (●) 250.0 °C isotherm, second experiment of this work.

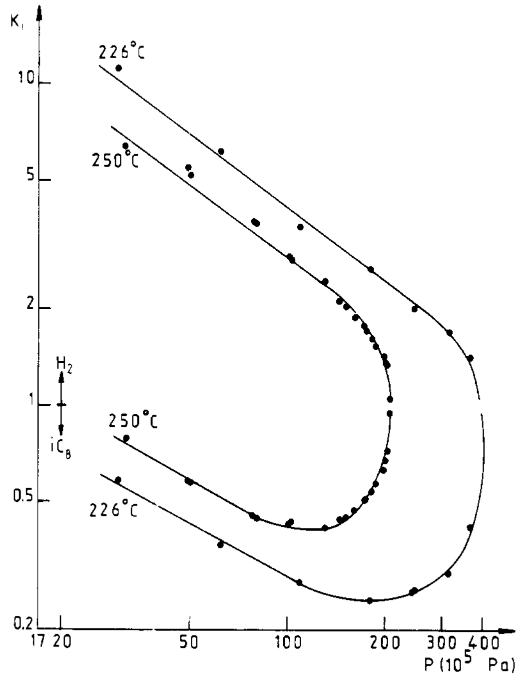

Figure 2. Partition coefficient for the system hydrogen-2,2,4-trimethylpentane: (+) ref 3; (●) present work.

Our experimental results are reported in Table II at two temperatures 226.0 and 250.0 °C. Figure 1 illustrates the comparison of present results at 226.0 °C with those of Peter and Reinhartz (*3*) at 226.2 °C. Agreement between the two sets of data is excellent for both bubble and dew curve. Our results show a less pronounced dispersion.

The mole fraction measurement is repeated at least three times. Deviation between these multiple measurements is always found to be less than 1.5%.

In determining the isotherm at 250.0 °C, we have tested the reproducibility of the results and validity of working in the critical region. As a test of reproducibility, two sets of data have been obtained by charging the cell with different amounts of 2,2,4-trimethylpentane. Figure 1 illustrates the results showing that all the experimental points lie on the same curve. It also shows that the critical region is well described by the present technique, allowing an evaluation of critical pressure.

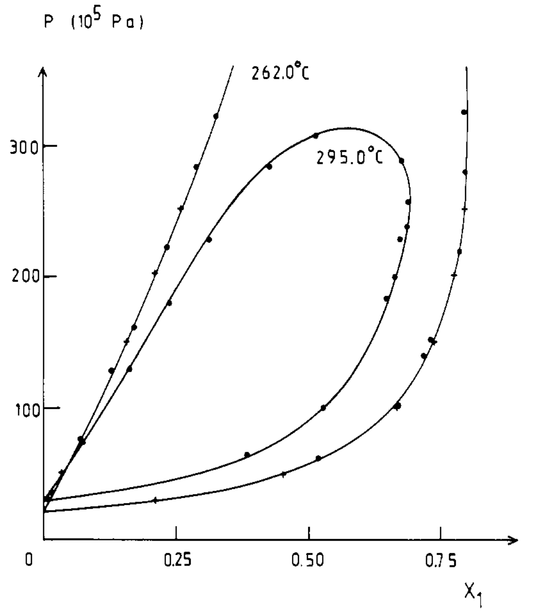

Figure 3. Vapor-liquid equilibrium data for the system hydrogen-toluene at 262.0 and 295.0 °C: (+) ref 5; (●) present work.

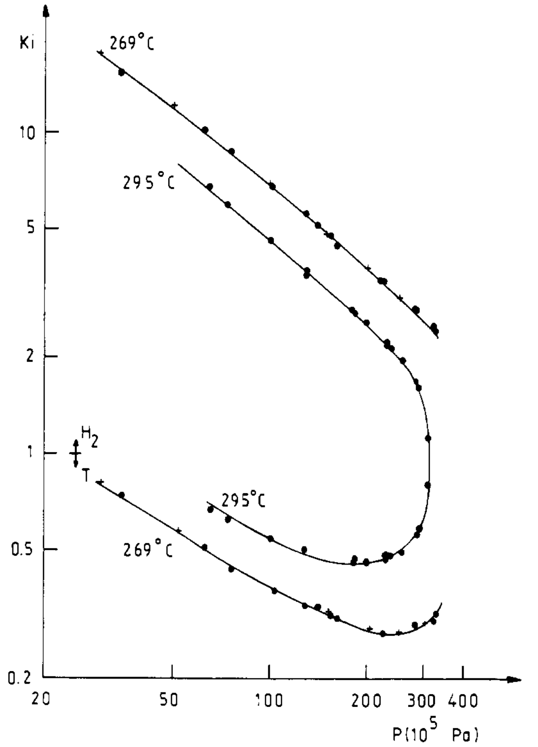

Figure 4. Partition coefficient for the system hydrogen-toluene: (+) ref 5; (●) present work.

For this system at 250.0 °C the critical pressure is $209 \times 10^5 \pm 2 \times 10^5$ Pa. From the extrapolation of the bubble curves to null hydrogen mole fraction the saturation vapor pressures of 2,2,4-trimethylpentane at each temperature can be found. These extrapolated values are close to those calculated from Antoine's equation (*4*) as shown in Table III. Partition coefficients, $k_i = Y_i/X_i$, appear in Figure 2 as functions of total pressure.

***Hydrogen-Toluene*.** This system has previously been studied by Simnick et al. (*5*) using a flow apparatus at four temperatures: 188.7, 229.0, 269.0, and 302.0 °C. We have chosen to re-

Table III. Saturating Vapor Pressure Data

hydrocarbon	T, °C	$10^{-5} \times P_S^{\circ}$,[a] Pa	$10^{-5} \times P_S^{\circ}$,[b] Pa	$10^{-5} \times P_S^{\circ}$,[c] Pa
2,2,4-trimethylpentane	226.0	13	13.3	
2,2,4-trimethylpentane	250.0	18	18.5	
toluene	269.0	21		21
toluene	295.0	28		28

[a] Extrapolated from our results. [b] From ref 4. [c] From ref 6.

Table IV. Vapor-Liquid Equilibrium Data for the System Hydrogen (1)-Toluene (2)

T, °C	$10^{-5}P$, Pa	x_1	y_1	k_1	k_2
269.0	34.6	0.019		15.0	0.729
269.0	62.3		0.521	10.0	0.505
269.0	76.0	0.070		8.57	0.430
269.0	103.0		0.668	6.68	0.369
269.0	129.0	0.128		5.56	0.330
269.0	140.5		0.718	5.02	0.329
269.0	153.5		0.733	4.70	0.316
269.0	162.0	0.172		4.36	0.302
269.0	222.5		0.789	3.40	0.275
269.0	223.0	0.232		3.40	0.276
269.0	281.0		0.796	2.78	0.286
269.0	284.0	0.289		2.77	0.281
269.0	323.0	0.327		2.45	0.297
269.0	327.0		0.792	2.39	0.311
295.0	64.5		0.385	6.64	0.653
295.0	74.0	0.074		5.85	0.615
295.0	101.0		0.527	4.54	0.535
295.0	130.0	0.162		3.66	0.488
295.0	180.5	0.237		2.76	0.452
295.0	184.0		0.648	2.69	0.464
295.0	200.0		0.665	2.52	0.455
295.0	229.5	0.311		2.20	0.461
295.0	230.0		0.673	2.16	0.475
295.0	239.0		0.686	2.11	0.475
295.0	257.0		0.689	1.93	0.484
295.0	284.5	0.415		1.64	0.545
295.0	289.0		0.675	1.57	0.569
295.0	308.0	0.514		1.20	0.791

produce the isothermal curve at 269.0 °C and to determine a new isotherm at 295.0 °C. The results are reported in Table IV and represented on Figure 3. Partition coefficients, K_i, are plotted on Figure 4 as a function of total pressure. Agreement between Simnick et al. measurements and ours is excellent up to the previous limit of 250 × 10^5 Pa. We have extended these results to higher pressure up to 370 × 10^5 Pa. The new isotherm at 295 °C is obtained even in the critical region with a critical pressure of 309 × 10^5 ± 2 × 10^5 Pa. Working in the critical region is possible because, in contrast to a flow method, a static method does not involve a continuous and fast phase separation.

Extrapolation of bubble curve gives the values of toluene saturation vapor pressure at each temperature. These are equal to those of Krase and Goodman (*6*), as shown in Table III.

Glossary

K_i	equilibrium partition coefficient for component i ($K_i = Y_i/X_i$)
P	total pressure, Pa
P_S°	saturating vapor pressure of pure component, Pa
T	temperature, °C
X_i	liquid mole fraction of component i
Y_i	vapor mole fraction of component i

Subscripts

1	hydrogen
2	hydrocarbon
S	value at saturation

Superscript

°	pure component

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