Vapor-Liquid Equilibrium in the *n*-Hexane–Nitrogen System

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Experimental vapor-liquid equilibrium data in the *n*-hexane–nitrogen binary system are presented. Equilibrium was established by using the vapor recirculation method over a pressure range from 17.01 atm. (250 p.s.i.a.) to 340.14 atm. (5000 p.s.i.a), and at temperatures from 37.78° C. (100° F.) to 171.1° C. (340° F.) in 156° C. (60° F.) increments.

IN THE study of the effect of nitrogen on the methane-*n*-hexane system, it was desirable to study the *n*-hexane-nitrogen binary system first. No data were found on this system over the pressure range from 250 to 500 p.s.i.a. and temperature range from 100° to 340° F.

EXPERIMENTAL

A stainless steel windowed glass cell with a volume of 35 cc. made by the Jerguson Valve and Gage Co. was charged with the reagents and equilibrium was attained at a desired constant pressure and temperature by recirculating the vapor from the top of the equilibrium cell through a magnetic piston pump into the bottom of the cell. Circulation of the vapor through the coexisting liquid phase was maintained for 2 hours except near the critical where 4 hours of circulation were necessary. A period of from 2 to 4 hours was found adequate for phase separation, depending on how close the particular run was to the critical.

The equilibrium cell was immersed in a 16-gallon oil bath which was maintained to within ±0.017° C. (0.03° F.) of a predetermined temperature by a Sargent temperature controller. Two mixers stirred the oil in the bath to provide consistent temperature as determined by four carefully placed thermocouples around the cell. The magnetic pump was located in an air bath which was maintained at, or slightly above, the oil bath temperature by a 750-watt strip heater, a circulating fan, and a Sargent off-on controller. The pressure of the system was determined to within ±2 p.s.i.a. by two Heise-Bourdon type gages which were periodically calibrated against a dead weight tester.

Analytical. Both the liquid and vapor phase at each experimental point were sampled for analysis. The samples were trapped between two needle valves in ¼-inch high pressure stainless steel tubing connected to the cell by way of ⅛-inch valves very near the cell. Before an experimental run was begun, the sample lines were filled with mercury flush with the inside of the cell. During sampling, the sample under cell pressure displaced the mercury in the sample lines. Mercury was added from the bottom of the cell to maintain constant pressure as sampling proceeded. About 1 cc. of vapor at system conditions was withdrawn from the top of the cell and expanded into previously evacuated 500-cc. glass flasks. The same procedure was followed for the liquid sample, except that only 0.1 to 0.2 cc. of liquid was withdrawn. The entire liquid sampling apparatus exterior to the oil bath was maintained above 66° C. (150° F.) by heating tape and a heating mantle around the flask.

The contents of each flask were then analyzed quantitatively on a Beckman GC-2A gas chromatograph which had been calibrated using the pure components. It was necessary to introduce the vaporized liquid sample into the chromatograph by using a special gas sample valve placed in an

Table I. Experimental Data

Temp., ° C. (° F.)	Pressure, Atm. (P.S.I.A.)	Mole Fraction N_2	
		Liquid phase	Vapor phase
37.78(100)	17.01 (250)	0.026	0.958
	34.01 (500)	0.053	0.981
	68.03(1000)	0.101	0.983
	102.04(1500)	0.137	0.989
	136.05(2000)	0.155	0.985
	170.07(2500)	0.190	0.988
	204.08(3000)	0.218	0.986
	238.10(3500)	0.253	0.984
	272.11(4000)	0.290	0.983
	306.12(4500)	0.330	0.975
	340.14(5000)	0.359	0.980
71.11(160)	17.01 (250)	0.025	0.904
	34.01 (500)	0.051	0.942
	68.03(1000)	0.099	0.964
	102.04(1500)	0.144	0.973
	136.05(2000)	0.182	0.973
	170.07(2500)	0.211	0.972
	204.08(3000)	0.244	0.964
	238.10(3500)	0.278	0.959
	272.11(4000)	0.311	0.958
	306.12(4500)	0.330	0.960
	340.14(5000)	0.391	0.958
104.4 (220)	17.01 (250)	0.023	0.789
	34.01 (500)	0.047	0.869
	68.03(1000)	0.095	0.921
	102.04(1500)	0.150	0.928
	136.05(2000)	0.199	0.928
	170.07(2500)	0.242	0.927
	204.08(3000)	0.283	0.926
	238.10(3500)	0.335	0.911
	272.11(4000)	0.380	0.899
	306.12(4500)	0.439	0.893
	340.14(5000)	0.479	0.867
137.8 (280)	17.41 (256)	0.021	0.614
	34.01 (500)	0.049	0.771
	68.03(1000)	0.105	0.835
	102.04(1500)	0.162	0.864
	136.05(2000)	0.220	0.882
	170.07(2500)	0.282	0.884
	204.08(3000)	0.342	0.884
	238.10(3500)	0.411	0.854
	272.11(4000)	0.507	0.816
	287.14(4221)	0.576	0.777
	287.07(4220)	0.601	0.772
	292.04(4293)	0.700	Single phase
	291.84(4290)	Critical	
171.1 (340)	34.01 (500)	0.049	0.567
	68.03(1000)	0.116	0.739
	102.04(1500)	0.192	0.765
	136.05(2000)	0.258	0.751
	170.07(2500)	0.331	0.740
	184.49(2712)	0.398	0.708
	196.05(2882)	0.485	0.693
	199.25(2929)	0.505	0.624
	200.68(2950)	Critical	

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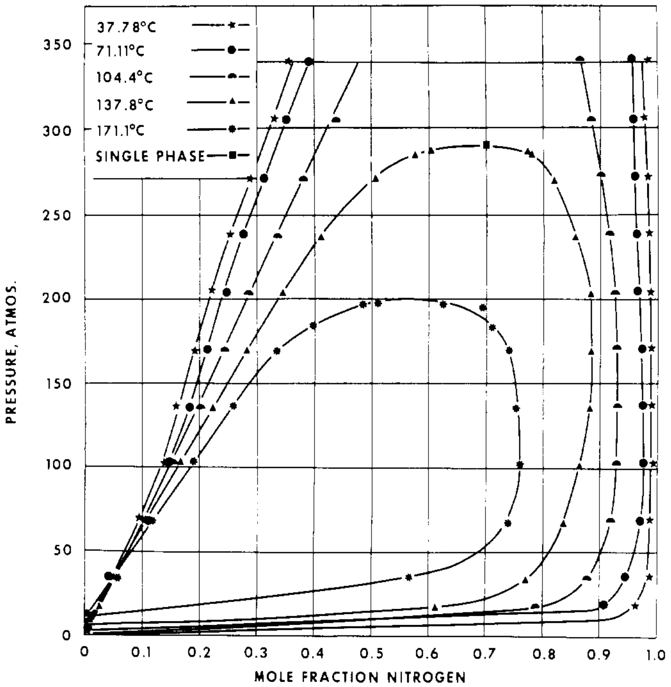

Figure 1. Vapor-liquid equilibria for the nitrogen–*n*-hexane system

air bath. This procedure prevented the possibility of condensation of the *n*-hexane, since the air bath was maintained above 66° C. (150° F.) and sample pressure in the flask was below 1 atm.

A unique two-column arrangement was employed utilizing an 8.0-foot Ansul ether column and a 3.5-foot molecular sieve column in series with switching valves, so that a complete analysis could be made in 8.5 minutes including a correction for any air leakage. No pressure or volume measurements were needed, once the instrument had been calibrated to analyze each sample and only one run per sample was necessary.

Many reruns and checks were made to ascertain that the instrument was properly calibrated and that the analysis was consistent. A mass spectrometer was used as an independent analytical instrument to check the gas chromatograph.

Materials Used. The *n*-hexane was research grade with a stated purity of 99.9%. The nitrogen was dry research grade with a purity of 99.85%. These purities were ascertained on both the gas chromatograph and the mass spectrometer.

RESULTS

The experimentally determined compositions of the coexisting vapor and liquid phases are listed in Table I and plotted in a pressure-composition diagram in Figure 1. The solubility of nitrogen in the liquid hydrocarbon phase increases with pressure, as was reported by several investigators (*1, 2, 3*).

ACCURACY

The over-all analytical procedure is thought to be reliable to ±0.002 mole fraction. Temperature variations within the cell were ±0.11° C. (0.2° F.) during circulation and ±0.028° C. (0.05° F.) during sampling and settling. The accuracy of the reported pressures is ±0.14 atm. (2 p.s.i.a.) during circulation, settling, and sampling.

LITERATURE CITED

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Vapor-Liquid Equilibrium Constants for the Ethane–*n*-Butane–*n*-Heptane System at 150°, 200°, and 250° F.

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Vapor-liquid equilibrium constants for the system, ethane–*n*-butane–*n*-heptane have been established at 150°, 200°, and 250° F. for pressures ranging from 450 p.s.i.a. up to the critical region. Values of critical pressure and composition have been obtained from these data and are presented for each temperature investigated.

CONSIDERABLE vapor-liquid equilibrium data extending into the critical region are presented in the literature for binary systems, but such information for mixtures containing more than two components is limited. To extend this information to the behavior of three-component systems, Herlihy and Thodos (*3*) and Mehra and Thodos (*7*) experimentally determined vapor-liquid equilibrium constants for the ethane-*n*-butane-*n*-pentane system at 150°, 200°, 250°, and 300° F. This type of study is being continued in the present investigation and deals with the ethane-*n*-butane-*n*-heptane system, which was selected for investigation because the three binaries of this ternary system have been comprehensively studied by Kay (*4,5,6*). Recent experimental vapor-liquid equilibrium constants are also reported by Mehra and Thodos for the ethane-*n*-butane and the ethane-*n*-heptane systems (*8,9*). Experimental K values for the ethane-*n*-butane-*n*-heptane system have been established in this investigation at 150°, 200°, and 250° F.