

Vapor-Liquid Equilibrium in the Methane-*n*-Hexane System

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The compositions of both equilibrium phases in the methane-*n*-hexane system have been determined at 37.78° C. (100° F.), 71.11° C. (160° F.), 104.4° C. (220° F.), 137.8° C. (280° F.), and 171.1° C. (340° F.), at total pressures from 17.01 atm. (250 p.s.i.a.) to 197.4 atm. (2902 p.s.i.a.). The critical pressure for each isotherm is reported.

ALTHOUGH a number of investigators have previously reported on the methane-*n*-hexane system (1, 2, 4, 5, 6) no compositions near the critical region were determined experimentally. In this paper the critical pressure at each isotherm was determined experimentally.

EXPERIMENTAL

A 35-cc. windowed glass cell was charged with the research grade reagents and equilibrium was established by recirculating the vapor from the top of the cell through the magnetic pump into the bottom of the cell for 2 hours. Near the critical, a period of 4 hours was used for recirculation. Settling times of 2 to 4 hours (depending upon the nearness to the critical) were used to assure complete phase separation before sampling. A detailed description of the apparatus and operating procedure is given by Roberts (3).

Analytical. Both the liquid and vapor phases at each equilibrium experimental point were sampled for analysis. Roberts (3) gives a detailed discussion of the sampling procedure. His sampling technique was modified only slightly to prevent condensation of the hexane as sampling took place. This was accomplished by placing heating tapes around the liquid sample lines exterior to the experimental apparatus and by placing a heating mantle around the 500-cc. glass flask in which the sample was trapped for analysis. Thermocouples were inserted around the sample lines and the lowest temperature was found to be 66° C. (150° F.), well above the boiling point for hexane at the partial pressure of hexane in any sample.

The composition of the coexisting liquid and vapor phases was determined on a Beckman GC-2A gas chromatograph which had been calibrated using the pure components. A unique two-column arrangement was used which allowed a complete analysis for the composition of a sample in one step. No pressure or volume measurements were necessary and corrections were obtained from the chromatogram for any air leak into the chromatographic or sampling systems.

The columns consisted of an 8-foot Ansul ether column (30% by weight on firebrick support) in series with a 3.5-foot molecular sieve column. Upon reaching the Ansul

ether column methane was separated from *n*-hexane, allowing methane to pass without retention into the molecular sieve column. Thermal conductivity detector response due to methane was received on a recorder. Then *n*-hexane which was still in the Ansul ether column was diverted through a capillary restrictor away from the molecular sieve column directly into the detector. The 0.005-inch i.d. capillary restrictor compensated for the pressure drop through the molecular sieve column, so that little base line disturbance occurred when the flow of the carrier gas was altered.

The instrument was calibrated with the pure components and with known compositions of methane and *n*-hexane to ascertain linear response. Checks were made on the mass spectrometer and agreement to within 1 mole % was attained. This analytical procedure is accurate to within 0.2 mole %.

Materials Used. The methane and *n*-hexane were of research grade supplied by Phillips Petroleum Co., with stated purity of 99.9%. Independent analyses on the mass spectrometer and the gas chromatograph proved the purity to be at least 99.9%.

RESULTS

A number of investigators have reported on the methane-*n*-hexane binary system. Frolich and others (2) measured the solubility of methane in *n*-hexane at 25.0° C. (77° F.) and at pressures as high as 88.44 atm. (1300 p.s.i.a.) with an estimated accuracy of 5%. Sage, Webster, and Lacey (4) reported the solubility of methane in *n*-hexane at 37.78° C. (100° F.), 71.11° C. (160° F.), and 104.4° C. (220° F.) and at pressures as high as 170.11 atm. (2500 p.s.i.a.). However, only three compositions were studied at each temperature, and no critical data were reported. Bubble point and dew point compositions at 25° C. (77° F.), 55° C. (131° F.), and 85° C. (185° F.), corresponding to pressures up to the critical pressures, were reported by Boomer and Johnson (1); however, the methane used contained 5.6% nitrogen. The solubility of methane in *n*-hexane corresponding to pressures up to the critical and at 37.93° C. (100.27° F.), 71.11° C. (160° F.), and 104.4° C. (220° F.) were determined by Schoch, Hoffmann, and Mayfield (5). Shim and Kohn (6) presented a very detailed vapor-liquid equilibrium investigation of the methane-*n*-hexane binary system between

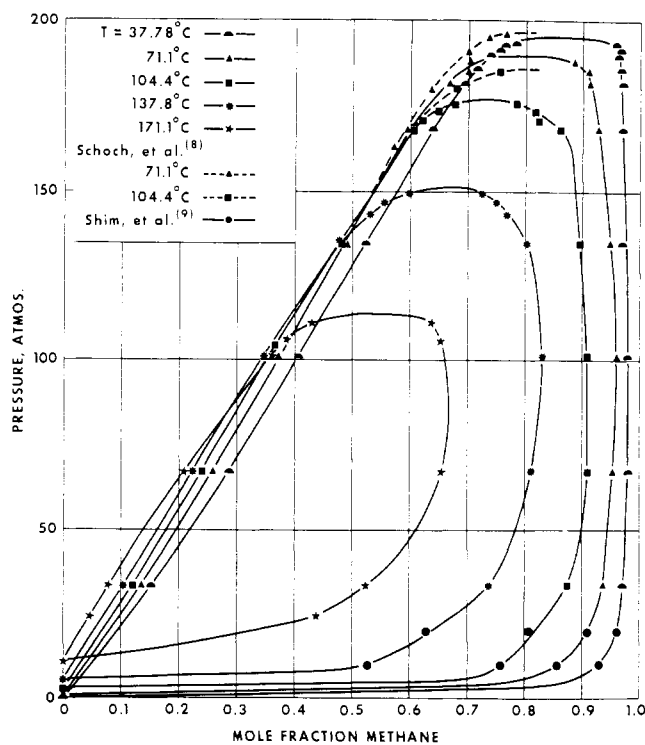
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Table I. Experimental Data

Temp., °C. (°F.)	Pressure, Atm. (P.S.I.A.)	Mole Fraction C_1	
		Liquid phase	Vapor phase
37.78(100)	34.01 (500)	0.153	0.969
	68.03(1000)	0.286	0.980
	102.04(1500)	0.404	0.979
	136.05(2000)	0.511	0.970
	170.07(2500)	0.638	0.969
	183.67(2700)	0.694	0.970
	188.10(2765)	0.715	0.968
	193.54(2845)	0.756	0.964
	192.18(2825)	0.740	0.962
	195.24(2870)	0.764	0.957
	197.41(2902)	Critical	
	71.11(160)	34.01 (500)	0.135
68.03(1000)		0.258	0.953
102.04(1500)		0.371	0.962
136.05(2000)		0.485	0.946
170.07(2500)		0.594	0.928
183.67(2700)		0.668	0.913
187.07(2750)		0.701	0.911
190.14(2795)		0.703	0.885
191.63(2817)		Critical	
104.4 (220)	34.01 (500)	0.119	0.871
	68.03(1000)	0.240	0.911
	102.04(1500)	0.351	0.908
	136.05(2000)	0.477	0.895
	170.07(2500)	0.604	0.861
	172.79(2540)	0.618	0.822
	175.51(2580)	0.650	0.817
	177.89(2615)	0.675	0.784
	178.37(2622)	Critical	
	137.8 (280)	34.01 (500)	0.103
68.03(1000)		0.223	0.811
102.04(1500)		0.345	0.830
136.05(2000)		0.477	0.803
144.90(2130)		0.528	0.768
148.30(2180)		0.556	0.751
151.16(2222)		0.598	0.725
152.86(2247)		Critical	
171.1 (340)	24.76 (364)	0.025	0.438
	34.01 (500)	0.079	0.522
	68.03(1000)	0.208	0.654
	102.04(1500)	0.363	0.660
	107.14(1575)	0.388	0.658
	111.09(1633)	0.422	0.641
	114.76(1687)	Critical	

-110° and 150°C., and up to a pressure of 160 atm. No compositions near the critical state were determined experimentally.

The data of Boomer (1), Sage (4), Schoch (5), and Shim (6) were compared with the data of the present study and reasonable agreement was obtained except for the critical temperatures reported by Schoch, 71.11°C. (160°F.), and 104.4°C. (220°F.), and the vapor compositions reported by Boomer. Schoch did not use a windowed glass cell in his work and he actually extrapolated a series of bubble point compositions to obtain his critical pressures. Small disagreements with Boomer's vapor composition data were also reported by Shim. The data obtained in this investigation

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

agree to within 0.5 mole % with data interpolated from Shim.

The compositions of the coexisting vapor and liquid phases are listed in Table I and a *P-X* diagram is presented in Figure 1. The solubility of methane in *n*-hexane decreases with temperature, as all investigators on this system have reported.

ACCURACY

The over-all analytical procedure is thought to be reliable to ± 0.002 mole fraction of the smoothed experimental data. Temperature variations within the cell were $\pm 0.11^\circ\text{C}$. (0.2°F .) during circulation and $\pm 0.028^\circ\text{C}$. (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.

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