To the best of our knowledge no other V^E data have been reported in literature for the binary mixtures considered here to compare our results.

Further thermodynamic investigations on these binary mixtures are under way.

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Vapor–Liquid Equilibrium in Methane + Quinoline Mixtures at Elevated Temperatures and Pressures

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Compositions of coexisting vapor and liquid phases at equilibrium were experimentally determined for mixtures of methane + quinoline in a flow apparatus at 189.6, 269.7, 349.5 and 429.7 °C. Measurements were made at seven pressures from 20 to 250 atm at each of the three lower temperatures and from 30 to 220 atm at the highest temperature.

Introduction

Gas–liquid equilibrium data of mixtures of methane and heavy solvents are of industrial and technological interest. Correlations of methane solubility and solvent volatility are depended upon for engineering design and analysis, and experimental data are needed for developing and checking correlations.

In this work we determine the compositions of coexisting equilibrium vapor and liquid phases of mixtures of methane + quinoline at elevated temperatures and pressures. No previous investigations of this mixture system have been reported in the literature. Sebastian et al. (*2*) reported the vapor pressure of quinoline and vapor–liquid equilibrium in mixtures of hydrogen + quinoline.

Experimental Section

The experimental apparatus and procedure of this study have been described (*3*). Attainment of equilibrium in the flow apparatus used has been examined with care in some of our previous reports (*1*, *3–5*).

As a result of experience gained in the operation of the apparatus, we have improved the control of temperature. Fluctuations of temperature of the equilibrium cell in the course of measurement of all the points on an isotherm were reduced to within 0.17 °C at the highest temperature and within 0.11 °C at the other three temperatures. The temperature of the preheated stream was controlled to within 0.5 °C of the equilibrium cell temperature.

Methane gas was supplied by Matheson with a purity of 99+%. Quinoline purchased from Fisher Scientific Co. is certified reagent grade of 99+% purity but showed a deep purple color. The color was removed and purity improved by vacuum fractional distillation over zinc as described by Sebastian and co-workers (*2*).

Table I. Vapor–Liquid Equilibrium Data for Mixtures of Methane + Quinoline

p, atm	x_M	y_M	K_M	K_Q
		189.6 °C		
19.91	0.0197	0.9815	49.82	0.0188
29.98	0.0296	0.9865	33.34	0.0139
49.9	0.0488	0.9901	20.28	0.0104
100.2	0.0945	0.9919	10.49	0.0089
149.4	0.1352	0.9919	7.33	0.0094
200.0	0.1750	0.9904	5.66	0.0117
249.7	0.2112	0.9888	4.68	0.0143
		269.7 °C		
19.90	0.0206	0.8876	43.09	0.1148
29.91	0.0311	0.9187	29.53	0.0839
50.0	0.0529	0.9449	17.86	0.0582
99.3	0.1036	0.9612	9.28	0.0433
152.4	0.1571	0.9643	6.14	0.0424
199.4	0.2025	0.9633	4.75	0.0460
249.1	0.2455	0.9622	3.92	0.0501
		349.5 °C		
19.83	0.0170	0.5838	34.34	0.4234
30.11	0.0304	0.7052	23.21	0.3040
49.8	0.0557	0.7999	14.35	0.2119
99.9	0.1191	0.8692	7.30	0.1485
151.3	0.1831	0.8866	4.84	0.1388
199.5	0.2410	0.8886	3.69	0.1468
249.0	0.3010	0.8837	2.94	0.1664
		429.7 °C		
30.03	0.0170	0.2716	15.98	0.7410
50.4	0.0514	0.4770	9.28	0.5514
99.9	0.1379	0.6381	4.63	0.4198
152.0	0.2283	0.6802	2.98	0.4144
175.2	0.2767	0.6752	2.44	0.4490
200.2	0.3311	0.6639	2.01	0.5025
220.2	0.4027	0.6391	1.59	0.6043

Samples were collected from the condensates of both the overhead and bottom cell effluents for all experiments and analyzed by gas chromatography. No significant products from decomposition were detected at any of the conditions studied.

Results and Discussion

The observed coexisting equilibrium phase compositions are reported in Table I. At the three lower temperatures, data were taken in the pressure range of 20–250 atm. The pressure range

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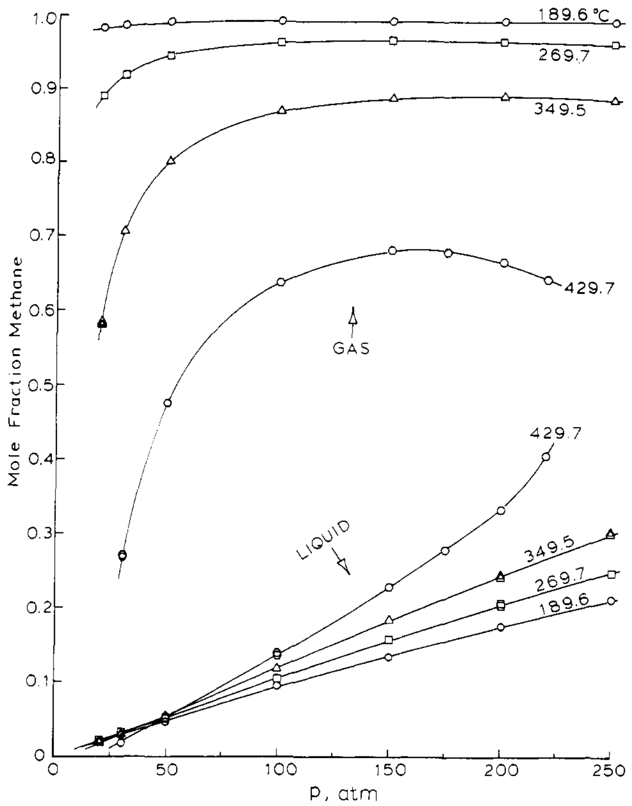

Figure 1. Equilibrium phase compositions for the methane + quinoline binary system.

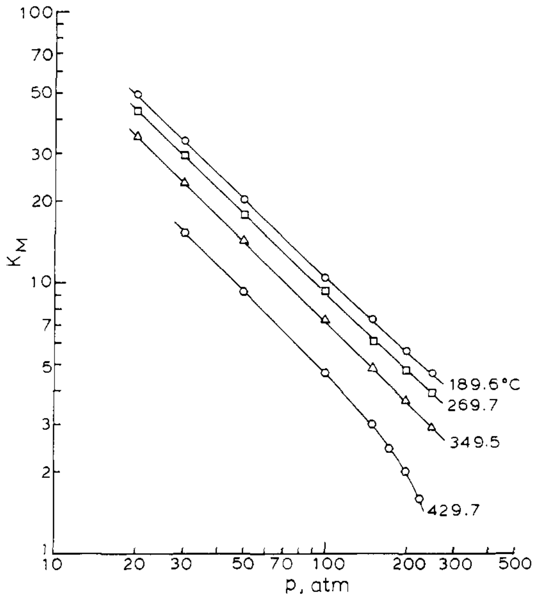

Figure 2. *K* value of methane in methane + quinoline.

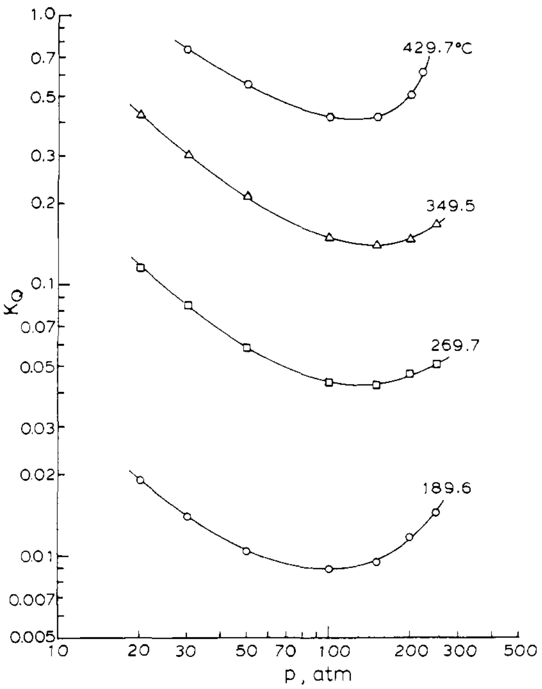

Figure 3. *K* value of quinoline.

at the highest temperature reported here was limited at the low-pressure side by excessive vaporization of quinoline and at the high-pressure side by close approach to the critical state. Seven pressures were observed at each isotherm. Two or three samples were taken at a condition of fixed temperature and pressure. The agreement among multiple samples at one condition is in general within 2% in the mole fraction of methane. Only the averaged values of the compositions are given in the table; the individual samples are shown in Figure 1 as separate points when they can be distinguished.

The mean values of *x* and *y* were used to calculate the equilibrium ratios of methane and quinoline. The results are presented in the table and shown in Figures 2 and 3. Close approach to the critical pressure of the mixture at 429.7 °C is clearly shown in the figures.

Glossary

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

Subscripts

M	methane
Q	quinoline

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