V vapor phase

Registry No. CCl_4, 56-23-5; CO, 630-08-0; CH_4, 74-82-8; CF_4, 75-73-0; SF_6, 2551-62-4; H_2, 1333-74-0; N_2, 7727-37-9; O_2, 7782-44-7; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9.

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Vapor-Liquid Equilibrium for Quinoline/Methanol and Tetralin/Methanol Mixtures at Elevated Temperatures and Pressures

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Vapor and liquid equilibrium compositions have been measured for binary quinoline/methanol and tetralin/methanol mixtures at 248, 276, and 307 °C and over a range of pressures from approximately 1.5 MPa up to the critical pressure of each binary mixture. The mixture critical pressures are also determined by visual observation of critical opalescence.

Introduction

Experimental data are presented for quinoline/methanol and tetralin/methanol mixtures. These results are the latest in a series of measurements of vapor-liquid equilibrium compositions for binary mixtures of model coal-derived compounds with methanol at elevated temperatures and pressures. Such data are needed for the development of coal conversion processes, particularly those which would use dense fluids (such as methanol, water, or toluene) as extractive solvents.

The experimental technique that is used for measuring equilibrium compositions has been described previously (*1*, *2*). Compositions are obtained by direct sampling of the equilibrium phases, and a view cell allows direct observation of all phase behavior, including critical phenomena. The apparatus is rated for temperatures as high as 425 °C and pressures up to 30 MPa.

Previous measurements of fluid-phase equilibria for binary mixtures of quinoline and tetralin with dense fluids are relatively scarce. Chao and co-workers have used a similar experimental technique to measure vapor and liquid equilibrium compositions for binary mixtures of quinoline and tetralin with hydrogen, carbon dioxide, and methane (*3-8*). Measurements were made at temperatures up to 430 °C and pressures to 25 MPa. Schneider and co-workers (*9*) have used a synthetic experimental technique to determine phase boundaries and critical

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Table I. Vapor-Liquid Equilibrium Data for Quinoline/Methanol

press., MPa	mole fraction methanol in	
	liquid	vapor
	T = 248.0 °C	
1.07	0.132	0.876
2.11	0.272	0.936
3.24	0.412	0.957
4.23	0.532	0.966
5.22	0.653	0.972
6.25	0.768	0.976
7.43	0.895	0.982
8.45	0.974	0.988
8.62	CP[a]	CP
	T = 276.3 °C	
1.59	0.149	0.855
2.87	0.271	0.913
4.21	0.388	0.936
5.41	0.498	0.947
6.76	0.609	0.954
8.03	0.709	0.957
9.38	0.818	0.957
10.12	0.868	0.954
10.72	CP	CP
	T = 306.6 °C	
1.91	0.129	0.775
3.32	0.229	0.861
4.81	0.338	0.889
6.22		0.910
6.31	0.440	
7.72	0.532	0.918
9.25	0.616	0.923
10.78	0.712	0.916
12.23	0.811	0.897
12.50	CP	CP

[a] CP = critical point.

curves for tetralin/water mixtures at temperatures up to 400 °C and at relatively high preessures (40–200 MPa).

Experimental Section

A flow technique is used to facilitate sampling at elevated pressures and to minimize thermal degradation of the hydrocarbon constituents by reducing residence times at elevated temperatures. The apparatus and experimental technique are essentially identical with those used to measure vapor–liquid equilibrium for 1-methylnaphthalene/methanol mixtures (*1*). One minor modification which has been made is the installation of 0.076-cm-i.d. × 25-m-long tubing in the forced convection nitrogen bath to preheat and mix the two-phase mixture entering the view cell. As before, the preheater/mixer heats the mixture to within 1 °C of the desired operating temperature.

Quinoline and tetralin with stated purities of 99% were obtained from Aldrich Chemical Co. Methanol with a stated purity of 99.9% was obtained from Fisher Scientific Co. These purity levels were verified by analysis on a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector. The chemicals were subsequently used without further purification; however, a dry nitrogen blanket was maintained over the feed solutions to prevent possible water absorption from the air.

Results

Table II. Vapor-Liquid Equilibrium Data for Tetralin/Methanol

press., MPa	mole fraction methanol in	
	liquid	vapor
	T = 248.1 °C	
1.59	0.110	0.832
2.69	0.211	0.897
3.76	0.305	
3.82		0.919
4.45	0.404	
4.86	0.453	0.931
5.45	0.550	
5.91	0.629	0.939
6.87	0.761	0.948
7.69	0.872	0.958
8.21	0.932	0.966
8.53	CP[a]	CP
	T = 276.4 °C	
1.56	0.074	0.704
2.79	0.159	0.822
4.10	0.272	0.870
5.42	0.384	0.897
6.67	0.489	0.904
7.83	0.607	0.910
9.16	0.723	0.908
9.96	0.814	0.897
10.16	CP	CP
	T = 306.6 °C	
1.77	0.072	0.596
3.01	0.149	0.738
4.31	0.238	0.799
5.76	0.329	0.832
7.14	0.417	0.848
7.43	0.436	0.850
8.43	0.502	0.855
8.66	0.520	0.854
10.16	0.629	0.847
11.07	0.708	0.822
11.29	CP	CP

[a] CP = critical point.

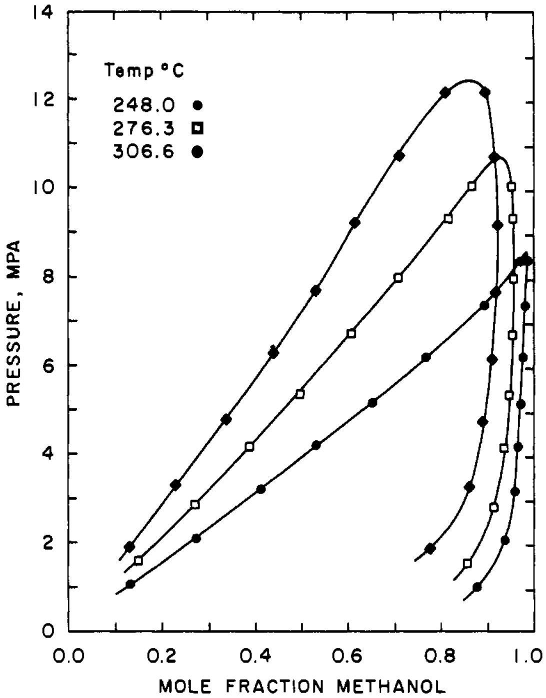

Figure 1. Measured equilibrium pressures and vapor and liquid compositions for quinoline/methanol mixtures at 248.0, 276.3, and 306.6 °C.

Vapor and liquid equilibrium compositions for quinoline/methanol and tetralin/methanol mixtures are given in Tables I and II, and shown on the pressure-composition diagrams in Figures 1 and 2, respectively. These compositions were determined with a Perkin-Elmer 3290B gas chromatograph equipped with a thermal conductivity detector and a 0.32 cm × 2 m Porapak "P" column, 80–100 mesh. The results represent averaged values of duplicate samples, and have an experimental uncertainty of 0.1–0.3 mol %. The reproducibility

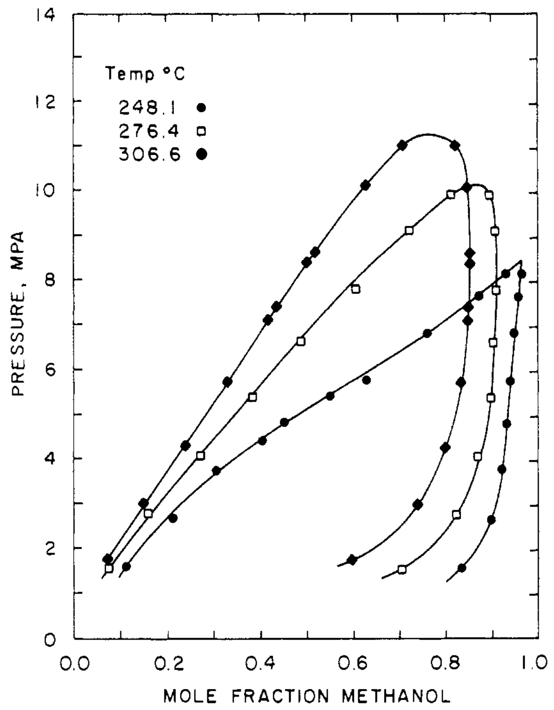

Figure 2. Measured equilibrium pressures and vapor and liquid compositions for tetralin/methanol mixtures at 248.1, 276.4, and 306.6 °C.

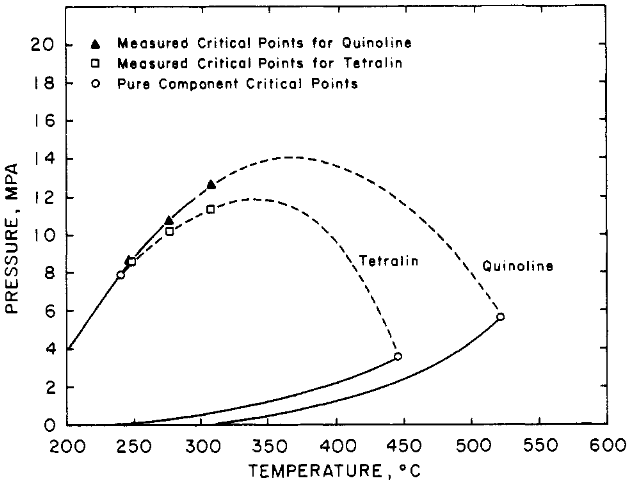

Figure 3. Pressure-temperature projection of gas-liquid critical curves for binary mixtures of quinoline and tetralin with methanol.

of a given sample ranged from 0.05 to 0.2 mol %. Mixture critical pressures that are also given in Tables I and II were determined by visual observation of critical opalescence. These values are accurate to ±0.03 MPa.

Previous work has established that equilibrium conditions are obtained with this flow technique (*1*, *2*). However, the results reported in this paper were also checked for equilibrium conditions by collecting samples at different flow rates. As before, measured compositions were found to be independent of flow rates within the experimental uncertainties stated above. No evidence of thermal degradation of any component was found from gas chromatographic analysis. It should be noted, however, that if quinoline or tetralin solutions were allowed to remain in the cell for a period of about 1 h during shutdown, they become dark in color. This observation emphasizes the need to minimize thermal degradation for these organic compounds at the temperatures of interest in this study.

Table III. Pure Component Critical Temperatures and Pressures (*12*, *13*)

component	critical temp, °C	critical press., MPa
methanol	240	8.1
tetralin	446	3.5
quinoline	509	3.8

The measured critical pressures for the two binary systems can be used to construct complete gas-liquid critical curves for each binary mixture. This was accomplished by using the calculational method of Heidemann and Khalil (*10*) with the Peng-Robinson equation of state (*11*). The calculated mixture critical curves are shown on the pressure-temperature projection in Figure 3. Pure component critical temperatures and pressures for all three mixture constituents are given in Table III. Both critical curves run continuously between the critical points of the two pure compounds and exhibit a pressure maximum. These results are similar to those obtained previously for the mixture critical curves of methanol with 1-methylnaphthalene, naphthalene, and 1-naphthol (*1*, *2*).

Registry No. MeOH, 67-56-1; quinoline, 91-22-5; tetralin, 119-64-2.

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