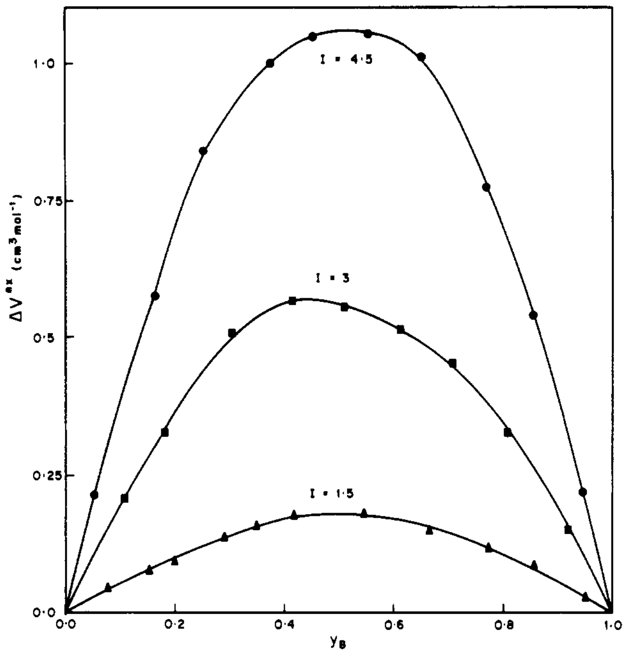

Figure 1. Excess volume of mixing (ΔV^{ex}) vs. y_B for aqueous KCl-$CaCl_2$ at 298.15 K.

and v_2 along with the standard deviation of fit.

In summary, it is shown that densities of aqueous electrolyte mixtures like KCl-$CaCl_2$-H_2O can be accurately predicted by the Pitzer's equation.

Use of mixing parameters helps in improving the estimation of densities. However, an attempt should be made to treat binary mixing terms independent of ionic strengths. This will help us in limiting the number of parameters necessary for predicting the density of such ternary mixtures.

Acknowledgment

The late C. V. G. Reddy's attempts in arranging the experimental facilities at NIO are gratefully acknowledged. I thank Professor Gordon Atkinson for introducing me to electrolytes.

Registry No. KCl, 7447-40-7; $CaCl_2$, 10043-52-4.

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Vapor-Liquid Equilibrium for 1-Naphthol/Methanol and Naphthalene/Methanol Mixtures at Elevated Temperatures and Pressures

Mark C. Thies and Michael E. Paulaitis*
Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Vapor and liquid equilibrium compositions have been measured for binary 1-naphthol/methanol and naphthalene/methanol mixtures at 248, 276, and 307 °C over a range of pressures from approximately 1.3 MPa to the respective mixture critical pressures. Mixture critical pressures are obtained by observation of critical opalescence within the view cell.

Introduction

The development of new processes for the conversion of nontraditional hydrocarbon resources to useful products will depend to a large extent on the availability of accurate chemical and physical property data. As part of our research program to study fundamental equilibrium phase behavior related to such conversion processes, we are measuring vapor-liquid equilibrium compositions for mixtures of model coal-derived compounds with dense fluids, such as methanol and water, at elevated temperatures and pressures. These data are of particular interest for coal conversion processes which use dense fluids as extractive solvents.

In this paper we report experimental results for two binary mixtures: 1-naphthol/methanol and naphthalene/methanol. The flow technique used for measuring equilibrium compositions has been described previously (*1*). Compositions are determined by sampling coexisting fluid phases, and phase behavior, such as critical phenomena, can be observed directly through a view cell. The apparatus is rated for temperatures as high as 425 °C and pressures up to 30 MPa.

Chao and co-workers have used a similar experimental technique to measure vapor-liquid equilibrium compositions for model coal-derived compounds with compressed gases (hydrogen, carbon dioxide, methane, nitrogen) at elevated temperatures and pressures (*2-4*). However, these investigations did not include naphthalene (mp = 80 °C) and 1-naphthol (mp = 95 °C), which are solids at ambient temperatures. Schneider and co-workers have used a synthetic experimental technique to determine the coexistence curves and critical curves for related water/hydrocarbon binary mixtures at elevated temperatures and high pressures (50-200 MPa). A limited number of measurements have been made for vapor-liquid equilibrium naphthalene/water mixtures (*5*).

Experimental Section

A flow technique is used to facilitate sampling at elevated pressures and to minimize thermal degradation of the hydro-

Table I. Vapor-Liquid Equilibrium Data for 1-Naphthol/Methanol

press., MPa	mole fraction methanol liquid	mole fraction methanol vapor
T = 247.8 °C		
1.14	0.202	0.970
1.77	0.277	0.978
3.00	0.418	0.985
4.21		0.987
4.31	0.580	
5.21	0.687	
5.45		0.989
6.24	0.807	0.989
7.33	0.896	0.990
8.30	0.972	0.992
8.69	CP[a]	CP
T = 276.3 °C		
1.76	0.194	0.951
3.01	0.340	0.971
4.38	0.464	0.977
5.60	0.563	0.979
6.94	0.656	0.980
8.18	0.744	0.980
9.69	0.849	0.979
10.85	0.902	0.974
11.24	CP	CP
T = 306.5 °C		
1.90	0.168	0.909
3.41	0.278	0.944
4.93	0.384	0.958
6.32	0.476	0.962
7.96	0.573	0.964
9.48	0.672	
9.51	0.679	0.965
10.93	0.737	0.961
11.00	0.739	0.961
12.50	0.818	0.952
13.48	0.875	0.928
13.65	CP	CP

[a] CP = critical point.

carbons by reducing residence times at elevated temperatures. Since 1-naphthol and naphthalene are solids at ambient temperatures, this experimental technique—which was described previously to measure vapor–liquid equilibrium compositions for 1-methylnaphthalene/methanol mixtures (*1*)—required slight modifications as described below.

1-Naphthol/Methanol. In order to feed 1-naphthol at ambient conditions to the high-pressure system, liquid mixtures consisting of up to 25 mol % 1-naphthol in methanol were prepared. These solutions were compressed and delivered with a Milton Roy Minipump (Model No. 396) at flow rates from 150 to 400 mL/h as before. A dry nitrogen blanket was maintained over the feed solution to prevent water absorption from the air.

At some compositions, precipitation of 1-naphthol from the liquid phase exiting the view cell would occur at temperatures which were below the operating temperature of the system. To prevent such precipitation, the line exiting the thermostated bath was heated with electrical tape and liquid solvent (1-butanol) was mixed in-line with the 1-naphthol/methanol mixtures at the micrometering valve after pressure letdown. The resulting 1-butanol/1-naphthol/methanol mixture formed a homogeneous solution at ambient conditions, which could be subsequently analyzed by gas chromatography.

Naphthalene/Methanol. The relatively low solubility of naphthalene in methanol at ambient conditions (about 5 mol %) prevented feeding naphthalene as a liquid mixture with methanol. Hence naphthalene was maintained as a liquid at approximately 100 °C and delivered to the high-pressure system as a compressed liquid with the Milton Roy Minipump. The pump head temperature was also maintained at 100 °C. An inert gas blanket was maintained over the liquid naphthalene at atmospheric pressure to prevent oxidation at elevated temperatures.

Since precipitation of naphthalene could occur from both the vapor and liquid phases exiting the thermostated bath, both lines exiting the bath were heated and toluene was pumped in-line into each phase at the micrometering valve after pressure letdown. Homogeneous liquid solutions were obtained and analyzed by gas chromatography.

Naphthalene and methanol with stated purities of 99.9+% were obtained from Fischer Scientific Co., and 1-naphthol with a stated purity of 99.8+% was obtained from Aldrich Chemical Co. The diluents—toluene (stated purity of 99.9%) and 1-butanol (stated purity of 99.8%)—were also obtained from Fischer Scientific Co. These purity levels were verified by gas chromatographic analysis, and the chemicals were used without further purification.

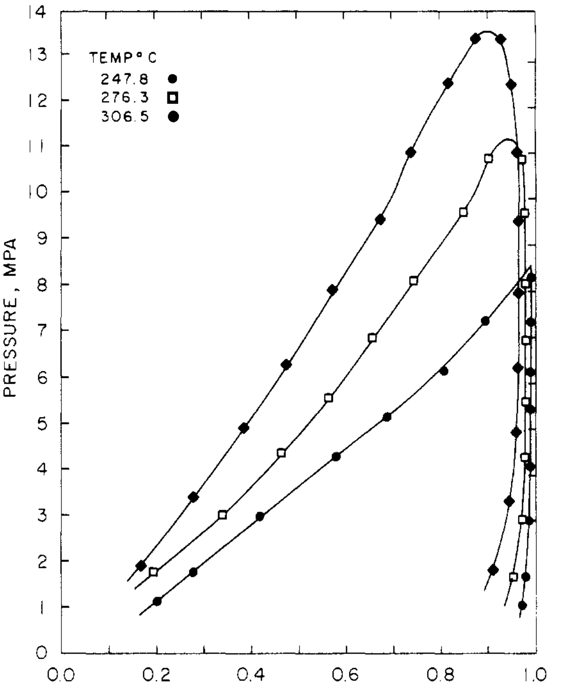

Figure 1. Measured equilibrium pressures and vapor and liquid compositions for 1-naphthol/methanol mixtures at 247.8, 276.3, and 306.5 °C.

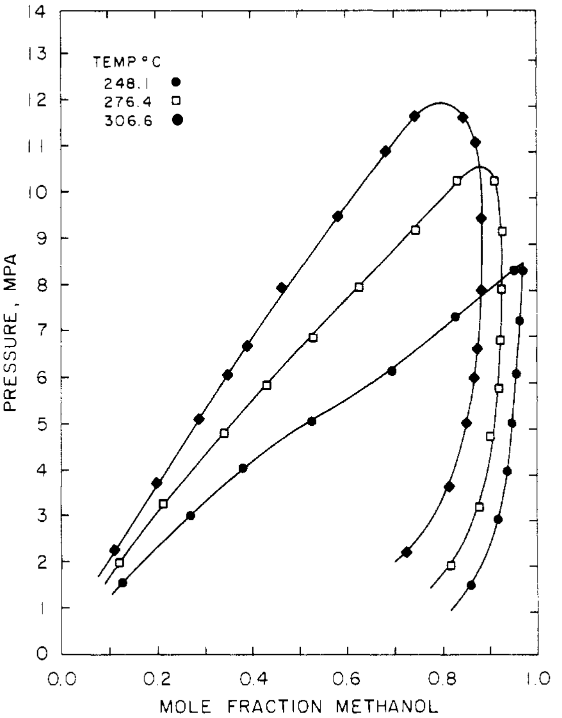

Figure 2. Measured equilibrium pressures and vapor and liquid compositions for naphthalene/methanol mixtures at 248.1, 276.4, and 306.6 °C.

Results

Measured compositions and corresponding pressures for binary 1-naphthol/methanol mixtures at 247.8, 276.3, and 306.5 °C are given in Table I and depicted on the pressure–composition diagram in Figure 1. The results for binary naphthalene/methanol mixtures at 248.1, 276.4, and 306.6 °C are

Table II. Vapor–Liquid Equilibrium Data for Naphthalene/Methanol

	mole fraction methanol			mole fraction methanol	
press., MPa	liquid	vapor	press., MPa	liquid	vapor
T = 248.1 °C			8.03	0.626	0.927
1.54	0.127	0.860	9.27	0.745	0.930
3.01	0.268	0.919	10.36	0.833	0.912
4.07	0.378	0.939	10.62	CP	CP
5.10	0.524	0.949			
6.21	0.693	0.959	T = 306.6 °C		
7.35		0.964	2.24	0.110	0.724
7.41	0.829		3.72	0.198	0.815
8.45	0.954	0.973	5.12	0.287	0.852
8.62	CP[a]	CP	6.09	0.348	0.868
			6.72	0.390	0.874
T = 276.4 °C			7.98	0.465	0.887
1.98	0.120	0.817	9.55	0.584	0.885
3.28	0.212	0.880	10.98	0.683	
4.83	0.341	0.903	11.19		0.873
5.87	0.431	0.920	11.74	0.743	0.846
6.93	0.529	0.922	12.07	CP	CP

[a] CP = critical point.

given in Table II and shown in Figure 2. The compositions were determined by analysis with a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector and represent average values obtained from triplicate samples. Reproducibility of a given sample was 0.1–0.4 mol %, and the experimental uncertainties in the measured composition are 0.1–0.5 mol %.

Mixture critical pressures are also noted in Tables I and II and were obtained by observation of critical opalescence. The reported values are accurate to ±5 psi. Our previous work established that equilibrium conditions were obtained with this flow technique (*1*). However, equilibrium conditions were also repeatedly checked during these experiments. Samples were collected at different flow rates and measured compositions were found to be independent of flow rate within experimental uncertainties. All flow rates were sufficiently high that no thermal degradation of the hydrocarbons was observed.

Discussion

The results obtained for naphthalene/methanol mixtures are similar to those obtained previously for 1-methylnaphthalene/methanol mixtures (*1*). Liquid-phase compositions at a given temperature and pressure are essentially the same for both systems. However, the mole fractions of naphthalene in the vapor phase are higher than those measured for 1-methylnaphthalene. This can be attributed to higher vapor pressures for pure naphthalene.

In contrast, the results obtained for 1-naphthol/methanol mixtures are significantly different than those obtained for naphthalene or 1-methylnaphthalene with methanol. Substantially higher methanol mole fractions in the liquid phase and lower 1-naphthol mole fractions in the vapor phase were measured. The latter results can be attributed to the relatively low vapor pressure for pure 1-naphthol.

A pressure–temperature projection depicting the gas–liquid critical curve for each binary mixture can be constructed from the measured critical pressure at each temperature. These critical curves are shown on one projection in Figure 3. For comparison, the mixture critical curve for benzene/methanol mixtures (*6*) is also shown. Since partially miscible liquids and three-phase, liquid–liquid–gas equilibrium were not observed in our experiments, we conclude that the naphthalene/methanol and 1-naphthol/methanol mixtures have continuous gas–liquid critical curves—similar to that for benzene/methanol mixtures—which connect the critical points for the corresponding pure components (see Figure 3). Unlike the critical curve for benzene/methanol mixtures, these two critical curves exhibit pressure maxima. The characteristic shape of the mixture critical curve and consequently the characteristic phase behavior for the binary mixture is directly related to the difference in critical temperatures for the two constituents (*7*). Similar pressure–temperature projections and phase behavior might be expected for mixtures of methanol with three- and four-ring aromatic compounds. However, the critical curves and two-phase regions for such mixtures would extend to higher pressures.

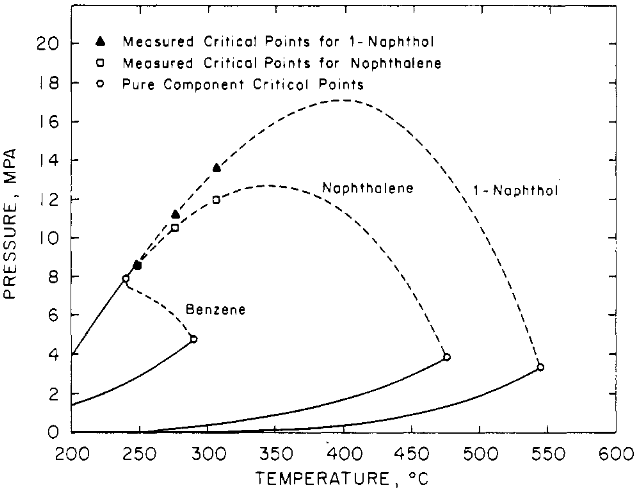

Figure 3. Pressure–temperature projection of gas–liquid critical curves for binary mixtures of benzene, naphthalene, and 1-naphthol with methanol.

The equilibrium phase behavior for mixtures of water with these aromatic compounds would be significantly different, since the critical temperature of water is substantially higher than that for methanol.

Registry No. Methanol, 67-56-1; 1-naphthol, 90-15-3; naphthalene, 91-20-3.

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