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# Vapor-Liquid Equilibrium for 1-Methylnaphthalene/Methanol Mixtures at Elevated Temperatures and Pressures

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Vapor and liquid equilibrium compositions have been measured for binary 1-methylnaphthalene/methanol mixtures at 246.4, 272.2, and 296.9 °C over a range of pressures from approximately 1.3 MPa to the respective mixture critical pressures. Mixture critical pressures are obtained by visual observation of critical opalescence within the view cell.

## Introduction

Experimental investigations of fluid-phase equilibria at elevated temperatures and pressures are relatively scarce for mixtures containing model coal compounds with dense fluids, such as water, methanol, or ammonia. Such information is important, however, for the design and evaluation of potential coal conversion processes in general and is of particular interest for potential conversion processes that could utilize these dense fluids as extractive solvents.

In this work, a new flow experimental technique is described for measuring equilibrium compositions, temperatures, and pressures for binary and multicomponent mixtures coexisting in two fluid phases at temperatures up to 450 °C and pressures up to 5000 psi. Measured vapor and liquid equilibrium compositions are reported for binary 1-methylnaphthalene/methanol mixtures at temperatures between approximately 250 and 300 °C, and at pressures up to the mixture critical point. The apparatus includes a view cell for observing phase equilibrium behavior. This visual capability is an important feature for measurements near the critical point and for determining mixture critical temperatures and pressures.

Chao and co-workers (1) have used a similar experimental technique to measure vapor-liquid equilibrium at elevated temperatures and pressures for binary mixtures containing model coal compounds, such as 1-methylnaphthalene, with supercritical gases, such as hydrogen (2), carbon dioxide (3), and methane (4). These investigators have published extensively on work involving several other model coal compounds with each of these supercritical gases and have more recently reported results for binary mixtures containing nitrogen (5), and ternary mixtures containing two supercritical gases (6). Their experimental method does not have viewing capabilities; however, a new flow method has been described which does include a view cell (7).

Wilson and Owens (8) have also reported using a flow technique with a view cell to measure vapor-liquid equilibrium at elevated temperatures and pressures for mixtures of coal liquids with hydrogen, methane, and hydrogen sulfide.

## Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. A flow technique is used to facilitate sampling at elevated pressures and to minimize thermal degradation by reducing residence times for the mixtures at elevated temperatures. Methanol and 1-methylnaphthalene are delivered as compressed liquids by separate high-pressure feed pumps (Milton Roy Model no. 396 Minipumps). The preheater/mixer consists of 0.635 cm i.d. tubing approximately 1 m in length which contains a helical steel ribbon to promote mixing and is wound with electrical tape to heat the mixture to within 1 °C of the desired operating temperature. The total constant flow rate from the two feed pumps ranges from 250 to 500 mL/h. The desired operating temperature is achieved by further heating in 0.076 cm i.d. tubing approximately 1.5 m in length which is located within the constant-temperature bath. The equilibrated, two-phase mixture is then fed to the view cell which functions as a phase separator. The gas or fluid phase of lower density subsequently exits at the top of the cell and is expanded to atmospheric pressure across a micrometering valve (Autoclave Engineers Model no. 30 VRM). The pressure letdown also results in cooling so that a liquid sample is collected. The liquid or fluid phase of higher density exits at the bottom of the cell and is expanded in a similar manner to ambient conditions. Compositions of both samples are determined by analysis with a Hewlett-Packard 5880A gas chromatograph utilizing a flame ionization detector.

The view cell was purchased from Jacoby-Tarbox Corp. and has been modified in our laboratory for operation above 100 °C. The cell consists of a 316 stainless steel enclosure with windows on opposite faces to enable observation along the entire vertical length of the inside of the cell. The cell windows are made of high-temperature aluminosilicate glass (Hoya Corp.) mounted on graphite gaskets with specially designed brass antiextrusion rings. The maximum operating conditions for the cell are limited by the windows and are estimated to be 450 °C at 5000 psi. The internal volume of the cell is approximately 60 cm$^3$.

The thermostat consists of a forced-convection, nitrogen bath sealed from outside air and surrounded by insulation. Vycor windows on opposite sides of the bath permit observation into the view cell. For the safety of the observer, a polycarbonate shield is also mounted over the viewing window. Heating is achieved by circulating the nitrogen across three Chromalox
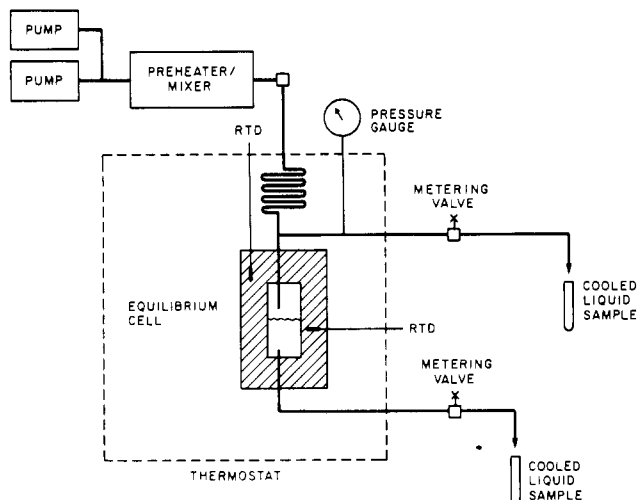
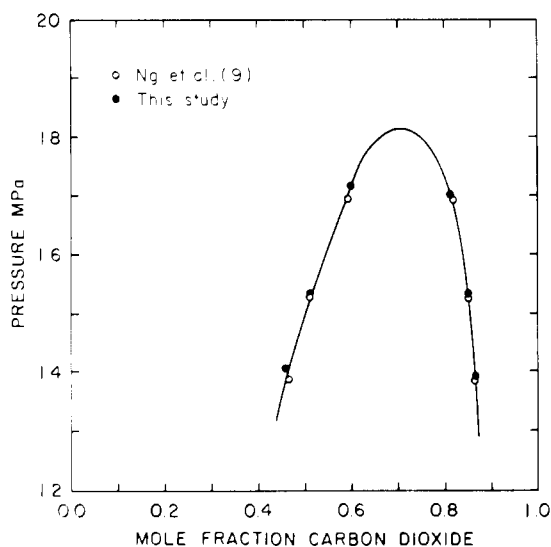**Figure 1.** Schematic diagram of the experimental apparatus.



**Figure 2.** Comparison of measured equilibrium pressures and vapor and liquid compositions for $m$-xylene/$CO_2$ mixtures at 202.6 °C with experimental results from Ng et al. (9).

strip heaters regulated by a Leeds and Northrup controller. Input to the controller comes from a 100Ω platinum resistance thermometer located within the bath. Thermal gradients within the bath are estimated to be less than 0.5 °C due to the turbulence generated by circulating nitrogen. Temperature variations in the view cell, however, are much smaller—i.e., less than ±0.04 °C.

Operating temperatures are measured with a platinum resistance thermometer inserted in the view cell wall, and a Keithley Model 191 digital multimeter. The thermometer and multimeter were calibrated as a unit by the National Bureau of Standards and are accurate to ±0.05 °C. System pressure is controlled to ±2 psi by adjusting the micrometering valves on the exit streams from the view cell. Pressure is measured with a Bourdon-type Heise gauge (Gregory Model CM, 0–10,000 psi range) calibrated against a Budenberg dead-weight gauge. The accuracy of the Heise gauge is 0.05% of the indicated pressure. Thus, for the moderate pressure range of interest in this work, the experimental uncertainty of the pressure measurements is ±2 psi.

The 1-methylnaphthalene (supplied by Aldrich Chemical Co.) was found to be 99+ mol% pure with the major impurity being 2-methylnaphthalene. The methanol with a 99.8+ mol% purity was supplied by Fischer Scientific Co. Both chemicals were used without further purification; however, a dry nitrogen blanket

**Table I. Measured Equilibrium Pressures and Phase Compositions for Binary $m$-Xylene/$CO_2$ Mixtures at 202.6 °C**

| press., MPa | [CO₂], mole fraction | |
| --- | --- | --- |
| | liquid | vapor |
| 13.96 | | 0.866 |
| 14.07 | 0.458 | |
| 15.38 | 0.512 | 0.851 |
| 17.06 | | 0.812 |
| 17.20 | 0.600 | |

**Table II. Measured Equilibrium Pressures and Phase Compositions for Binary Methanol/1-Methylnaphthalene Mixtures** [a]

| press., MPa | [MeOH], mole fraction | |
| --- | --- | --- |
| | liquid | vapor |
| *T* = 246.4 °C | | |
| 1.31 | 0.103 | |
| 1.34 | | 0.911 |
| 2.71 | 0.243 | |
| 2.74 | | 0.951 |
| 4.10 | 0.394 | |
| 4.14 | | 0.962 |
| 5.21 | 0.537 | |
| 5.31 | | 0.969 |
| 6.25 | 0.699 | |
| 6.36 | | 0.972 |
| 7.07 | 0.809 | |
| 7.14 | | 0.974 |
| 7.17 | 0.820 | |
| 7.85 | 0.913 | |
| 7.87 | | 0.978 |
| 8.25 | 0.956 | |
| 8.31 | 0.959 | 0.983 |
| 8.58 | CP | CP |
| *T* = 272.2 °C | | |
| 1.50 | 0.104 | |
| 1.54 | | 0.862 |
| 1.61 | | 0.867 |
| 2.91 | 0.205 | |
| 3.00 | | 0.925 |
| 4.39 | 0.325 | |
| 4.61 | | 0.942 |
| 5.87 | 0.465 | |
| 6.04 | | 0.950 |
| 7.54 | 0.611 | |
| 7.60 | | 0.952 |
| 9.13 | 0.766 | |
| 9.18 | | 0.952 |
| 10.04 | 0.848 | |
| 10.14 | | 0.945 |
| 10.32 | | 0.939 |
| 10.36 | 0.877 | |
| 10.55 | CP | CP |
| *T* = 296.9 °C | | |
| 1.91 | 0.109 | |
| 1.95 | | 0.831 |
| 3.31 | 0.204 | |
| 3.34 | | 0.885 |
| 4.58 | 0.287 | |
| 4.62 | | 0.908 |
| 6.14 | 0.379 | |
| 6.36 | 0.391 | 0.925 |
| 8.41 | 0.541 | |
| 8.45 | | 0.928 |
| 9.27 | 0.605 | 0.927 |
| 10.93 | 0.735 | 0.920 |
| 11.73 | | 0.903 |
| 11.79 | 0.800 | |
| 12.07 | CP | CP |

[a] CP = critical point.

was maintained over the methanol feed reservoir to prevent absorption of water from the air. No evidence of thermal degradation of either component could be found by gas-chro-
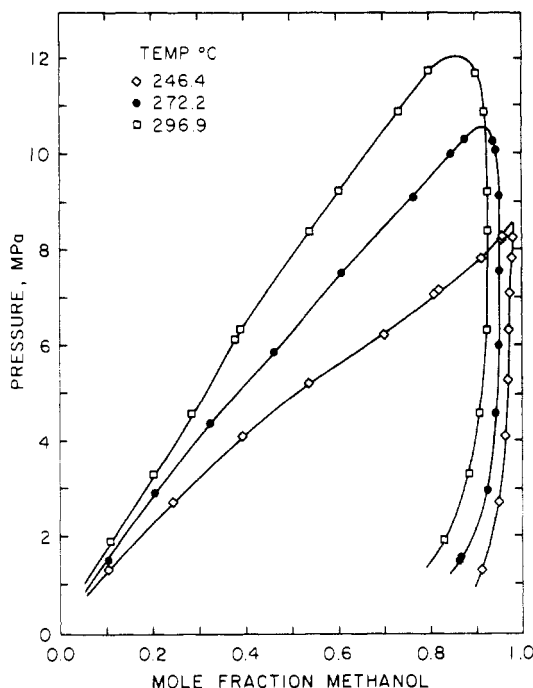
**Figure 3.** Measured equilibrium pressures and vapor and liquid compositions for 1-methylnaphthalene/methanol mixtures at 246.4, 272.2, and 296.9 °C.

matographic analysis after experimental runs at elevated temperatures.

**Results**

Vapor and liquid equilibrium compositions have been measured for two binary mixtures: $m$-xylene/carbon dioxide and 1-methylnaphthalene/methanol. Measuremetns of equilibrium pressures and phase compositions for binary $m$-xylene/carbon dioxide mixtures at 202.6 °C have been made for comparison with previously reported data of Robinson and co-workers (9). The results obtained in this work are given in Table I, and compared with the existing data in the pressure-composition diagram of Figure 2. The comparison shows very good agreement between our results using the flow experiment and those obtained by Robinson and co-workers using a static method.

Measurements of equilibrium pressures and phase compositions for binary 1-methylnaphthalene/methanol mixtures at

246.4, 272.2, and 296.9 °C are given in Table II and shown in the pressure-composition diagram of Figure 3. The reported compositions represent average values obtained from duplicate samples which are reproducible to within 0.3 mol%. The uncertainties in measured compositions are within 0.1-0.4 mol %. The higher uncertainties are associated with 1-methylnaphthalene compositions greater than 20 mol %.

Mixture critical pressures reported in our results are obtained by observation of critical opalescence and are considered accurate to within ±5 psi. During an experiment, the phase behavior is monitored visually to confirm that equilibrium exists within the cell. Bubbling in the liquid phase or condensation in the gas phase provides definitive indications of perturbations from equilibrium conditions which are evident several minutes before the temperature and pressure readings indicate such phenomena. These visual capabilities become increasingly important for measurements approaching the critical point where such perturbations from equilibrium are more likely to occur. As an additional check for equilibrium conditions, samples were collected for different flow rates at the same operating temperature and pressure. Measured compositions were found to be independent of flow rate, within the experimental uncertainties reported above.

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# Solubilities of Cholesterol, Sitosterol, and Cholesteryl Acetate in Polar Organic Solvents

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**Solubilities of cholesterol, sitosterol, and cholesteryl acetate are reported at various temperatures ranging from 11 to 50 °C in methanol, ethanol, acetone, acetonitrile, and 2-propanol and in some aqueous mixtures of these solvents. The solubilities of these steroids are represented by best-fit equations for each solvent.**

**Introduction**

It is well-known that cholesterol is an etiologic agent in artherosclerosis diseases (1, 2) while sitosterol lowers cholesterol concentration in the blood (3). These diseases are also known to be related to the crystal habit of the two steroids (4). In a recent study we have found that the crystal habit is in turn