

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

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Vapor and liquid equilibrium compositions have been measured for the tetralin/toluene system at 573, 603, 633, and 672 K at pressures ranging from the vapor pressure of tetralin to the binary mixture critical pressure at each temperature. Mixture critical pressures were obtained by visual observation of critical opalescence within the view cell and have been used to establish the gas-liquid critical curve for this system.

Introduction

Experimental data are presented for binary mixtures of tetralin and toluene. These results are an extension of previous work at the University of Delaware, which focused on binary mixtures of methanol with model coal-derived compounds (1-3). Such information is needed for the development of coal conversion processes, particularly those which would use dense fluids as extractive solvents. In this paper, we shift our attention to another dense fluid, toluene. This solvent has been used for a number of bench-scale investigations involving the supercritical extraction of coal (4, 5) and was the solvent of choice for a pilot plant operated by the National Coal Board of England in the late 1970s (6).

An equilibrium flow apparatus for measuring both vapor-liquid and liquid-liquid equilibrium compositions at temperatures up to 700 K and pressures to 250 bar has been constructed at Clemson. Equilibrium compositions are determined by direct sampling of the coexisting fluid phases. A central feature of the apparatus is a view cell for observing phase equilibrium behavior. This visual capability is an important asset for measurements near the critical point and for determining mixture critical pressures.

No previous measurements for this system at elevated temperatures and pressures are known. The vapor-liquid equilibria of binary mixtures of tetralin or toluene with light gases such as hydrogen, methane, and carbon dioxide have been determined by several investigators at temperatures up to 700 K and pressures to 250 bar (7-10). Schneider and co-workers (11) have used a synthetic method to determine the liquid-liquid critical curve for the tetralin/water system from the three-phase line to very high pressures (2000 bar).

Experimental Method

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 of the tetralin by reducing residence times for the mixtures at elevated temperatures. Toluene and tetralin are delivered as compressed liquids by separate high-pressure feed pumps (Milton Roy Model No. 396 Minipumps). The total constant flow rate from the two feed pumps ranges from 150 to 250 mL/h. The preheater/mixer is located in the thermostat and consists of three sections of stainless steel tubing. Two sections have an o.d. of 0.16 cm and an i.d. of 0.076 cm, and are approximately 15 m in length. The sections are interconnected by 0.32 cm o.d., 0.16 cm i.d. tubing approximately 3 m long to enhance mixing of the two phases. An in-line, Type J thermocouple is used to monitor the temperature of the mixture exiting the preheater/mixer and was

always read to within 1 K of the temperature in the view cell. The equilibrated, two-phase mixture from the preheater/mixer 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. 60VRMM). 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 gas chromatograph.

The view cell is a Model 11-T-20 liquid level gauge (Jerguson Gage and Valve Co.) which has been modified in our laboratory for high-temperature, high-pressure operation. The original cell body was replaced with one made in our laboratory from Carpenter 450 stainless steel. Its fluid chamber has been machined to the original height and depth but is reduced in width from 1.6 to 0.95 cm. The cell windows are made of high-temperature aluminosilicate glass (Hoya Corp.) mounted on graphite gaskets. Belleville washers of 17-7 PH stainless steel (Associated Spring) are used on the cover plate bolts to compensate for thermal expansion effects and to maintain sealing at elevated temperatures. The maximum operating conditions of the cell are estimated to be 700 K at 250 bar. The internal volume of the cell is approximately 30 cm³.

The thermostat consists of a forced-convection, nitrogen bath sealed from outside air and surrounded by insulation. Pyrex windows on opposite sides of the bath permit observation into the view cell. Heating is achieved by circulating the nitrogen across three Chromalox strip heaters regulated by a Leeds and Northrup controller. Input to the controller comes from a 100-ohm platinum resistance thermometer located within the bath. Thermal gradients within the nitrogen bath are estimated to be less than 0.5 K.

Several safety features are incorporated into the bath. A polycarbonate shield is mounted over the viewing window; the opposite window is intentionally unprotected and serves as a blowout port into a blank wall. To eliminate the possibility of an explosion, the composition of the gas phase in the bath is monitored by gas chromatography and is maintained by nitrogen purge to less than 1% oxygen. An on/off temperature controller (Fenwal Co.) which uses a Type J thermocouple serves as an independent high-temperature shutoff.

Materials

Tetralin with a stated purity of 99% and ACS reagent grade toluene were obtained from the Aldrich Chemical Co. The chemicals were analyzed with a Hewlett-Packard 5890 A gas chromatograph equipped with a flame ionization detector and a 530 μ m i.d. \times 5 m long methylsilicone column and were found to be 99.4 and 99.9% pure, respectively. In addition, analysis of the materials by Karl Fischer titration indicated that they contained no more than 0.02% water. Both chemicals were subsequently used without further purification.

Experimental Measurements

Operating temperatures of each phase in the cell are measured by two Type J thermocouples, which are inserted directly into the fluid chamber of the cell (Figure 1). The thermocouple

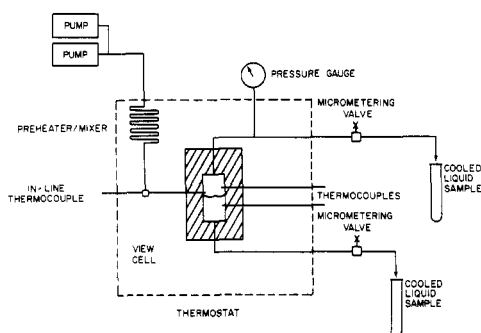


Figure 1. Schematic diagram of the experimental apparatus.

wires undergo a large temperature gradient as they pass through the walls of the thermostat and are therefore carefully secured to ensure reproducible results. Thermocouple voltage output is to a Keithley Model 191 digital multimeter. The thermocouples and multimeter were calibrated as a unit to an accuracy of ± 0.05 K with a Rosemount 162CE platinum resistance temperature standard (RTD), a Leeds and Northrup (L&N) Mueller temperature bridge (Model No. 8069-B), and an L&N dc null detector (Model No. 9828). The calibration of the RTD is traceable to the National Bureau of Standards. Temperature gradients in the view cell as measured by the two thermocouples were always found to be less than 0.1 K.

The operating pressure is controlled to better than ± 1 psi by adjusting the micrometering valves on the exit streams from the view cell. Pressure is measured with a Bourdon-tube type Heise gauge (Model CM, 0–1000 psi range) which had been calibrated against a Budenberg dead weight gauge (Model 380H) to an accuracy of 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 ± 1 psi.

Samples were analyzed with a Hewlett-Packard (HP) 5750B gas chromatograph equipped with a flame ionization detector and an HP 3392A integrator. Separation of the components was achieved with a 3.18 mm \times 1.8 m stainless steel column packed with 10% SP-2100 on 100–120 mesh Supelcoport (Supelco Co.).

Results

Vapor and liquid equilibrium compositions for tetralin/toluene mixtures at 573.0, 602.8, 632.9, and 672.3 K are given in Table I and shown on a pressure vs composition diagram in Figure 2. The results represent averaged values of duplicate samples and have an experimental uncertainty of 0.1–0.3 mol %. The reproducibility of a given sample ranged from 0.05 to 0.2 mol %. Temperatures in the view cell varied somewhat according to the flow rate and are accurate to ± 0.15 K. The measured vapor pressures of the pure components are in agreement with those reported in the literature (7, 12–15). Mixture critical pressures which are shown were obtained either by slowly raising the pressure from the two-phase region or by slowly lowering the pressure from the supercritical region until critical opalescence was observed. The reported values are the average of several measurements and are believed to be accurate to ± 0.10 bar.

Previous work in an apparatus of similar design has established that equilibrium conditions are obtained with this flow technique (1–3). However, the compositions reported in this paper were also checked for equilibrium by collecting samples at different flow rates. The effect of a wide range of flow rates on the equilibrium compositions at 602.8 K and 21.8 bar is shown in Table II.

No evidence of thermal decomposition of either component at any temperature or flow rate was found from gas chromatographic analysis. The attempts of previous investigators to

Table I. Vapor-Liquid Equilibrium Properties for the Tetralin/Toluene System

mole fracn toluene in			mole fracn toluene in		
press., bar	liquid	vapor	press., bar	liquid	vapor
$T = 573.0$ K					
5.94	0.000	0.000	18.63	0.550	0.792
7.56	0.081	0.250	21.01	0.641	0.838
9.08	0.149	0.396	23.35	0.724	0.877
11.18	0.242	0.526	25.90	0.808	0.915
13.56	0.346	0.650	28.40	0.883	0.949
16.32	0.463	0.737	30.59	0.946	0.974
18.56	0.551	0.795	32.90	1.000	1.000
$T = 602.8$ K					
9.15	0.000	0.000	24.87	0.517	0.726
11.53	0.088	0.237	28.08	0.605	0.780
13.94	0.166	0.382	31.66	0.698	0.830
16.70	0.261	0.505	35.35	0.788	0.875
19.91	0.365	0.611	39.66	0.880	0.918
21.80	0.423	0.658	42.38	CP ^a	CP
$T = 632.9$ K					
13.84	0.000	0.000	31.94	0.472	0.637
17.04	0.097	0.221	35.52	0.556	0.693
20.39	0.188	0.365	39.38	0.635	0.736
24.08	0.285	0.482	42.59	0.703	0.758
27.39	0.366	0.560	43.76	CP	CP
31.18	0.457	0.630			
$T = 672.3$ K					
22.04	0.000	0.000	39.24	0.356	0.442
25.83	0.081	0.153	40.66	0.384	0.457
29.83	0.168	0.272	42.59	CP	CP
34.18	0.252	0.363			

^a CP = critical point.

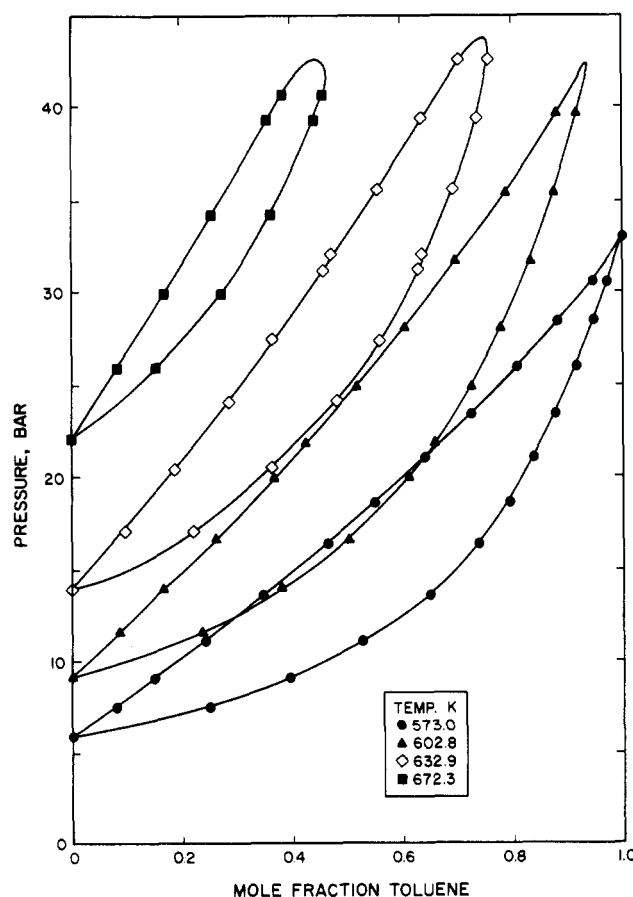


Figure 2. Measured equilibrium pressures and vapor and liquid compositions for tetralin/toluene mixtures at 573.0, 602.8, 632.9, and 672.3 K.

Table II. Measured Equilibrium Compositions and Flow Rates at 602.8 K and 21.80 bar

tot flow rate, mL/h	mole fracn toluene in	
	liquid	vapor
100	0.423	0.659
150	0.421	0.655
200	0.421	0.655
250	0.423	0.656
300	0.425	0.658
350	0.421	0.659
400	0.423	0.655

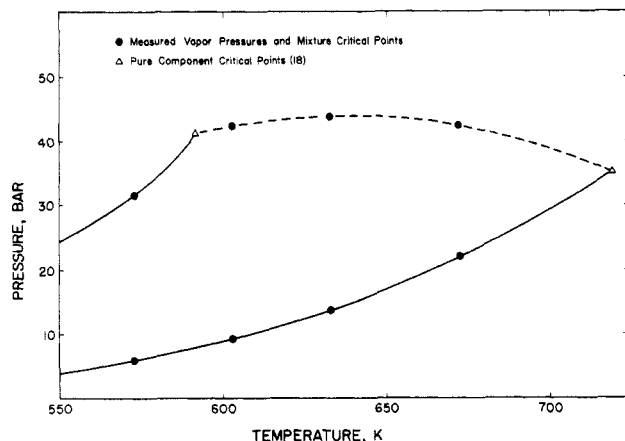


Figure 3. Pressure-temperature projection of gas-liquid critical curves for the tetralin/toluene system.

measure VLE at elevated temperatures for systems containing tetralin (16) clearly indicate the need for a flow technique for this type of study.

The measured vapor pressures and critical pressures can be used to construct the complete gas-liquid critical curve for this

system (see Figure 3). The gas-liquid critical curve is continuous and exhibits a shallow pressure maximum (17). For the methanol/tetralin system which was previously studied, the critical curve exhibits a more pronounced pressure maximum (3).

Registry No. Tetralin, 119-64-2; toluene, 108-88-3.

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Solubility of Cycloparaffins in Distilled Water and Salt Water

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Solubilities of cyclopentane, cyclohexane, methylcyclohexane, and cycloheptane were measured in distilled water and salt water (34.5 parts of NaCl per thousand parts of water). The salt water solubilities were correlated by the polar solubility parameter method. A method for predicting salt water solubility from known distilled water solubility was developed.

Introduction

The transport and fate of organic chemicals released into the environment is a major concern today for environmental protection. Leakage of gasoline from underground storage tanks is a good example of current interest. Solubility of the leaked materials is one of the physical chemical properties that determines the transport rate of the pollutants in the environment.

This paper describes experimental measurements of solubility of cycloparaffins of the molecular weight range found in gaso-

line. Most of the measurements were at 25 °C. Solubility was determined in distilled water for comparison with the literature values and in sodium chloride solutions having salinity in the range of sea water.

Experimental Section

The experimental approach was an adaptation of the method used by Polak and Liu (1). Hydrocarbon was equilibrated with water in 40-mL vials fitted with Teflon-lined septa. Water (~20 mL) was placed into the vial first. The vial was inverted and hydrocarbon was injected by means of a hypodermic needle into the space above the water. A second needle in the air space allowed air to escape as hydrocarbon was injected.

The vials were placed in inverted position in a constant temperature bath controlled to within ± 0.1 °C. Except for occasional gentle swirling no agitation was done. After about 2 weeks the water and hydrocarbon layers had equilibrated, and the water layer was analyzed to determine hydrocarbon solubility.