Title
LIQUID-LIQUID EQUILIBRIA FOR WATER-TOLUENE-PHENOL MIXTURES AT 150 AND 200° C

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Liquid-Liquid Equilibria for Water-Toluene-Phenol Mixtures at 150 and 200°C.

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ABSTRACT

Mutual solubilities at the three-phase equilibrium pressure have been measured for ternary aqueous mixtures containing toluene and phenol. The equilibrium compositions of both liquid phases and the three-phase equilibrium pressures are reported in the temperature range 150 - 200°C.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
Introduction

Water-hydrocarbon phase behavior is of fundamental interest in the chemical, petroleum, and synthetic-fuels industries. Mutual solubility data are required for design and operation of processes where there is contact between water and hydrocarbon or petrochemical streams. Often these processes are operated at elevated temperatures and pressures, where the organic-rich stream may contain a large number of components including water-soluble hydrocarbon derivatives. Mutual solubility data are especially important for design of water-pollution abatement processes.

While much is known about binary mutual water-hydrocarbon solubilities at near-ambient temperatures, few high-temperature data are available. Experimental data are scarce for aqueous ternary systems at high-temperatures.

We report here mutual solubilities for ternary aqueous mixtures containing toluene and phenol at 150 and 200°C. Mutual solubilities of water and phenol have been measured to the consolute point (Sorensen and Arlt, 1979), and water-toluene solubilities were recently measured to 200°C (Anderson and Prausnitz, 1986). Vapor-liquid equilibria for toluene-phenol mixtures have been reported in the range 100-180°C (Gmehling et al, 1982). Thus, phase-equilibrium data are available for each of the binary pairs in the water-toluene-phenol system; however the ternary has not previously been studied.

Experimental

Equilibrium measurements were made in a recirculating static apparatus; details of the equipment and of the sampling procedure are given elsewhere (Anderson and Prausnitz, 1986). The upper temperature limit of the apparatus is 250°C (corresponding to the maximum rating of the sampling valves). Room conditions define the lowest temperature attainable.

Accurate sampling of water and hydrocarbon liquid phases is difficult because of low mutual solubilities. Trace contamination of one phase with small droplets or dispersions of the other phase can cause large errors (Tsonopolous and Wilson, 1983). High-temperature measurements are especially prone to error because small
perturbations during sampling (e.g., temperature or pressure drops) can cause phase separation and significantly alter sample compositions (Anderson and Prausnitz, 1986). Our apparatus is designed to minimize temperature and pressure gradients during sampling.

To measure the full range of equilibrium compositions at a given temperature, mixtures of different overall composition are prepared in the equilibrium cell. In principle, it is not possible exactly to reproduce our measurements because the withdrawal of liquid-phase samples alters the overall cell composition. The resulting composition change for the equilibrium liquid phases is on the order of 1-2%; the least volatile component (phenol) is always present in greater concentrations for repeated samples.

**Chemicals**

Phenol was purchased from Aldrich Chemical Co. with a specified purity of 99+% and spectral-grade purity toluene was purchased from Mallinkrodt Co. Water was filtered and purified through a Millipore system before use.

**Analysis**

Water-rich and hydrocarbon-rich samples are both analyzed on a Varian Model 3700 gas chromatograph with a thermal-conductivity detector. Components are separated on a 1/8-inch x 6-ft stainless-steel column packed with 80/100-mesh Porapack Q. Relative responses of the components are calibrated against samples of known composition; details of the calibration procedure are given by Anderson (1985).

Samples to be analyzed (whether from the cell or for calibration) are vaporized into evacuated 1-liter stainless-steel cylinders. The cylinders are heated (in the sampling oven) to 200°C which ensures complete vaporization of all components. Each sample is analyzed at least three times. For the non-aqueous phase, relative responses of all components are reproducible to better than ±2%. In the aqueous phase, analyses for phenol and toluene are reproducible to ±5%, while water
response can be replicated to ±1%.

Results

Table 1 presents mutual solubilities of water-toluene-phenol mixtures at 150 and 200°C. The measured three-phase equilibrium pressures are also reported. In a ternary mixture this pressure depends not only on the temperature, but also on the liquid-phase compositions. We control the overall cell composition, which, at a given temperature, fixes the liquid-phase compositions and the three-phase pressure.

Figures 1 and 2 show ternary phase diagrams for water, toluene and phenol at 150 and 200°C. Tie lines were measured over the entire two-phase region, coming as close to the plait point as possible. While no ternary data are available for comparison, our results do approach the correct limit at low phenol concentrations as determined by the mutual solubilities of toluene and water. The water-rich region of the ternary diagrams is expanded in Figure 3. Again, the correct boundary condition appears to be met at low phenol concentrations.

Figure 4 presents the distribution of phenol between aqueous and non-aqueous phases for the two temperatures studied. At all concentrations, at 150°C phenol partitions more heavily into the organic-rich phase than at 200°C.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Literature Cited


TABLE 1

Water(1)-toluene(2)-phenol(3) mutual solubilities in mole percent at 150 and 200°C

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Liquid-Liquid Equilibria for the Water-Toluene-Phenol System at 150°C

Figure 1
This Work

Mutual solubilities of water and toluene at 200°C (Anderson & Prausnitz, 1983)

Liquid-Liquid Equilibria for the Water-Toluene-Phenol System at 200°C

Figure 2
Solubility of toluene in water at 150°C and 200°C (Anderson & Prausnitz, 1983)

○ 150°C
■ 200°C

Equilibrium Compositions of the Aqueous Phase for the Water–Toluene–Phenol System at 150°C and 200°C

Figure 3
Distribution of Phenol Between Aqueous Phase and Hydrocarbon-Rich Phase at 150°C and 200°C

Figure 4
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