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Fluid Phase Equilibria 230 (2005) 121–130
FLUID PHASE EQUILIBRIA
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Liquid–liquid equilibria for pseudoternary systems: isooctane–benzene–(methanol + water)

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Received 30 April 2004; received in revised form 7 December 2004; accepted 8 December 2004
Available online 21 January 2005

Abstract

Liquid–liquid equilibrium data are presented for the pseudoternary systems isooctane–benzene–(90 mass% methanol + 10 mass% water) at 298.15 K and isooctane–benzene–(80 mass% methanol + 20 mass% water) at 298.15 and 308.15 K, under atmospheric pressure. The experimental tie-line data obtained define the binodal curve for each one of the studied systems which depending on the amount of water present show type I or type II liquid–liquid phase diagrams. In order to obtain a general view of the effect of water on the partitioning of methanol and hence on the size of the two-phase region we have also determined experimentally 'isowater' tolerance curves for the system isooctane–benzene–methanol at 298.15 K, hence the tie-line data were also obtained for the ternary system. The experimental tie-line data for the four systems studied were correlated with the NRTL and UNIQUAC solution models obtaining a very good reproduction of the experimental behaviour.

Keywords: Experiments; Hydrocarbons; Isowater curves; Liquid–liquid equilibrium; Methanol; Tie-lines

1. Introduction

In recent years, there has been an increasing demand to use oxygenated compounds in the reformulation of gasoline in order to substantially reduce toxic emissions into the environment and simultaneously enhance the octane number of gasoline. The physical and chemical properties of methanol make it an excellent candidate as an oxygenated fuel additive. Some advantages obtained from using methanol are: its anti-knocking properties, high oxygen content, it can be produced from a relatively large variety of carbon-based feedstocks and relatively low cost. However, methanol presents partial miscibility with aliphatic hydrocarbons, not so with aromatics. Additionally, in the reformulation of gasoline, the presence of water, even in traces, should always be considered. Hence, the knowledge of the effect of water on the partial miscibility of methanol in mixtures of aliphatic and aromatic hydrocarbons is of interest from both the scientific and the technological points of view. It is therefore of utmost importance to undertake the creation a reliable body of experimental results on the liquid–liquid phase equilibrium of systems composed of methanol and different hydrocarbons representative of gasoline with the principal aim, apart from the intrinsic interest of the study of liquid–liquid phase diagrams of multi-component systems, of establishing the concentration interval of both hydrocarbons and methanol in which the two-phase region does not exist with and without the presence of water at a given constant temperature, under atmospheric pressure. Part of the same objective is to gain knowledge on the effect of temperature on the partitioning of methanol between the equilibrium phases.

In this work we chose to study the liquid–liquid equilibrium related to the study of the solubility of methanol mixed with different amounts of water in mixtures of two hydrocar-

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doi:10.1016/j.fluid.2004.12.003

bons: isooctane and benzene. We have investigated the phase equilibrium of the systems isooctane–benzene–(90 mass% methanol + 10 mass% water) at 298.15 K and isooctane–benzene–(80 mass% methanol + 20 mass% water) at 298.15 and 308.15 K. Although the results of this work correspond to quaternary systems, we present them as pseudoternary systems. The experimental tie-line data for the different pseudoternary systems and for the ternary system without water were successfully correlated with the NRTL and UNIQUAC solution models. Also, with a view to establish the general effect of water on the liquid–liquid behaviour of the ternary system composed of isooctane–benzene–methanol we have determined experimentally the solubility regions or 'isowater' tolerance curves at 298.15 K.

2. Experimental

2.1. Materials

The samples of methanol and benzene were supplied by Baker, whereas isooctane was provided by Sigma Aldrich. All the samples were HPLC grade and their purity is reported by the supplier to be higher than 99 mol%. They were used without any further purification. No impurities were detected using gas chromatography with a thermal conductivity detector (TCD), except for isooctane, which was necessary to distill in an all glass column at high reflux in order to eliminate impurities. The water used was deionized. The hydrocarbon samples were stored over sodium whereas methanol was stored over molecular sieve spheres. The amount of water in each pure sample was monitored along the time it took to carry out the present study with a Karl–Fisher apparatus, Aquatest 8, Photovolt. Methanol was the only compound that had water; it contained a maximum of 3×10^{-3} mass% of water.

2.2. Measurement of water tolerance or cloud point curves

The experimental measurement of water tolerance curves or 'isowater' curves was carried out in glass cells, similar to the ones used also in this work for the study of the liquid–liquid equilibrium. Fig. 1 shows a schematic diagram of a cell. The experimental procedure is the same as that described in previous work [1] based on the work by Briggs and Comings [2]. In a first stage the liquid–liquid phase diagram of the ternary isooctane–benzene–methanol system was determined as explained in the next section. About 10 cm^3 of a homogeneous ternary mixture of known concentration is placed in the glass cell and vigorously stirred by a coated magnetic bar. Then, water was added slowly from a syringe and stirring was applied almost continuously until the cloud point was observed. The mass of water added to reach the cloud point of the system was determined from mass differences with an analytical balance, Sartorious 2006 MP,

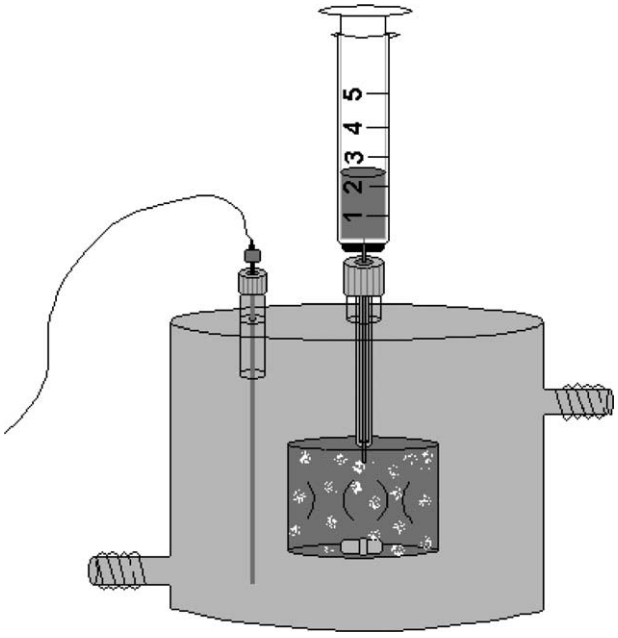

Fig. 1. Liquid–liquid equilibrium cell for the determination of water tolerance curves.

with a precision and accuracy of ±0.0001 g. This procedure was repeated as many times as necessary to obtain enough cloud points results that mapped out the whole region above the binodal curve of the corresponding ternary system. The temperature of the cell was controlled with a constant temperature bath-circulator at the temperatures reported in this work with a stability of ±0.01 K, as measured with a digital thermometer with platinum resistance probe.

Starting with five completely miscible binaries of isooctane–benzene of known constant mass ratio, i.e. isooctane/benzene = 85/15, 75/25, 60/40, 45/55, 30/70, 15/85 and 5/95, different known amounts of methanol were added in order to have 35 ternary miscible mixtures with different well-known concentration. The mass of each component of the binaries was determined in 10 cm^3 vials using the same analytical balance as above whereas that of methanol was determined by mass difference in the same analytical balance. The total miscible range of the ternary system was covered with 35 experimental points, including several cloud points for the binary benzene–methanol mixture. With all the known values of the concentration of the ternary miscible mixtures and the results corresponding to the amount of water added to observe the cloud point in each ternary mixture a plot of mass of water versus mass of methanol was prepared to obtain different curves each one identified by the mass% ratio of isooctane to benzene. From this plot different constant mass of water values were selected in order to interpolate enough values to fully describe the water tolerance behaviour and report isowater values as mass of water per 10 g of the ternary system.