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(Liquid + liquid) equilibria for the quaternary system water + methyl *tert*-butyl ether + ethanol + benzene at 303.15 K

Mónica B. Gramajo de Doz*, Alicia M. Cases, Horacio N. Sólimo

Departamento de Física, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán,
Av. Independencia 1800, 4000 Tucumán, Argentina

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Abstract

Tie line data for the ternary system water + methyl *tert*-butyl ether + ethanol, were obtained at $T = 303.15$ K. A quaternary system containing these three compounds and benzene was also studied at the same temperature. In order to obtain the binodal surface of the quaternary system, four quaternary sectional planes with several ratios of benzene and ethanol were studied. The distribution of methyl *tert*-butyl ether between the aqueous phase and the organic one was also analysed. For the ternary system, the distribution coefficients decrease from the plait point until reaching the value corresponding to the mutual solubility. A relationship between the mass fraction of methyl *tert*-butyl ether in the aqueous phase and the concentration of the mixture (ethanol + benzene) in the global composition was also obtained. From the experimental results we conclude that the concentration of methyl *tert*-butyl ether in the aqueous phase generally decreases when the sum (ethanol + benzene) in the global composition increases for the quaternary sectional planes. Furthermore, the liquid–liquid data for the ternary system were used to obtain interaction parameters for the NRTL and UNIQUAC activity coefficient models.

Keywords: Data; Liquid–liquid equilibria; Quaternary system; Distribution curve

1. Introduction

As part of an on going research program, we focus on the investigation of the phase equilibrium of quaternary systems containing hydrocarbons (benzene, isooctane, toluene, or cyclohexane), oxygenated compounds (methanol, ethanol or methyl *tert*-butyl ether), and water [1–6], because this type of systems has gained importance due to the increasing demand of oxygenated compounds to produce lead-free gasoline. The US Environmental Protection Agency recommends the use of alcohols (particularly ethanol) as gasoline additives to provide antiknock properties and to help reduce harmful combustion emissions [7,8]. One of the most widely used oxygenated compounds in reformulated gasoline is presently methyl *tert*-butyl ether (MTBE).

Since water is always present in commercial gasoline distribution tanks [9,10], even in traces, it always needs to be considered in the study of LLE for this type of systems. The knowledge of how the oxygenated compound is distributed between the aqueous phase and the organic phase is of particular interest.

Therefore, the aim of this work was to study the influence of the concentration of ethanol in the global composition on the distribution of the MTBE in the quaternary system water + methyl *tert*-butyl ether + ethanol + benzene: $[w_1\mathrm{H_2O} + w_2\mathrm{C_5H_{12}O} + w_3\mathrm{C_2H_6O} + w_4\mathrm{C_6H_6}]$. w_i is the mass fraction of component i.

Having this in mind, (liquid + liquid) equilibrium (LLE) measurements for this quaternary system and one of its ternary subsystems: $[w_1\mathrm{H_2O} + w_2\mathrm{C_5H_{12}O} + w_3\mathrm{C_2H_6O}]$ at $T = 303.15 \pm 0.05$ K and atmospheric pressure were performed. Data for the other two partially miscible ternary systems: $[\{w_1\mathrm{H_2O} + w_3\mathrm{C_5H_{12}O} + w_4)\mathrm{C_6H_6}\}$ and $\{w_1\mathrm{H_2O} + w_3\mathrm{C_2H_6O} + w_4\mathrm{C_6H_6}\}]$ were taken from previous works [2,6]. This particular temperature was selected because it is representative of tropical and subtropical climates.

The experimental data for ternary system were correlated with the UNIQUAC [11] and NRTL [12] models.

LLE data at 288.15 and 298.15 K and atmospheric pressure have been previously reported for the $[w_1\mathrm{H_2O} + w_2\mathrm{C_5H_{12}O} +$

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* Corresponding author. Tel.: +54 381 4364093; fax: +54 381 4363004.
E-mail address: mgramajo@herrera.unt.edu.ar (M.B. Gramajo de Doz).

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$w_3C_2H_6O$] system [13]. Comparing these results with ours, a little dependence with temperature within the temperature range 288.15–303.15 K was observed.

2. Experimental

2.1. Materials

Water was bidistilled in an all-glass apparatus. Methyl *tert*-butyl ether (considered as the solute throughout this work), ethanol, and benzene were supplied by Riedel de Haën in the first case and by Merck in the others. The purity of the chemicals was verified chromatographically, showing that their mass fractions were higher than 0.998. Therefore, they were used without further purification. The water content of these organic chemicals was periodically verified during the time of the study, using a Mettler DL18 Karl Fischer Titrator with an uncertainty of ±0.3%, and never surpassed 0.002 mass%. These chemicals were stored over 0.3 nm molecular sieves to prevent water absorption.

2.2. Methods

Before obtaining the LLE results for the quaternary system, one of its partially miscible ternary systems was studied while data for the other two were taken from the literature [2,6]. Ternary or quaternary mixtures of known overall composition within the heterogeneous region were prepared by weighing, using several 16 mL chromatographic vials as equilibrium cells. These vials were equipped with cap, septa, and Teflon coated magnetic stirrer bars to provide an intense and continuous stirring for at least 7 days using multipoint magnetic stirrers. After phase equilibrium was reached, the magnetic stirrers were turned off and both liquid phases were allowed to settle for 24 h before sampling, as previously reported [2]. The chromatographic vials were filled up to approximately 90% of their volumes in order to maintain the vapour space at a minimum.

At the end of each experiment, samples were taken from both phases with hypodermic syringes and analysed by means of gas chromatography. The internal standard method was applied to obtain quantitative results. Acetone (C_3H_6O) (Merck, chromatographic quality) with a mass fraction purity > 0.999 (GC) was the standard compound used for this purpose. First, the needle was introduced through the septa in order to take samples of the upper phases. They were immediately added to known amounts of the internal standard, placed in 2 mL chromatographic vials. Samples of the lower phases were then taken introducing the needle and blowing air while it went through the upper phase in order to avoid its contamination. Before adding the sample to the internal standard, the needle was dried with tissue paper and the mixture was analysed in the same way as the upper phase. A Hewlett Packard 6890 gas chromatograph with an automatic injector (Agilent G2613A) directly connected to a ChemStation (HP G2070AA) was used. Good separation of the five components was obtained on a 30 m long × 0.25 mm i.d. × 0.5 μm film thickness capillary column (INNOWax, cross-linked polyethylene glycol, HP 19091N-233). The temperature program used was: initial temperature 343 K for 2 min, ramp 50 K min^{-1}, and final temperature 393 K for another one and a half minute. The nitrogen carrier gas flow rate was electronically kept constant working with a split ratio of 20:1 and with the injector maintained at 453 K. Detection was carried out by a thermal conductivity detector at 523 K. Three or four analyses were performed for each sample in order to obtain a mean mass fraction value with a repeatability better than 1%.

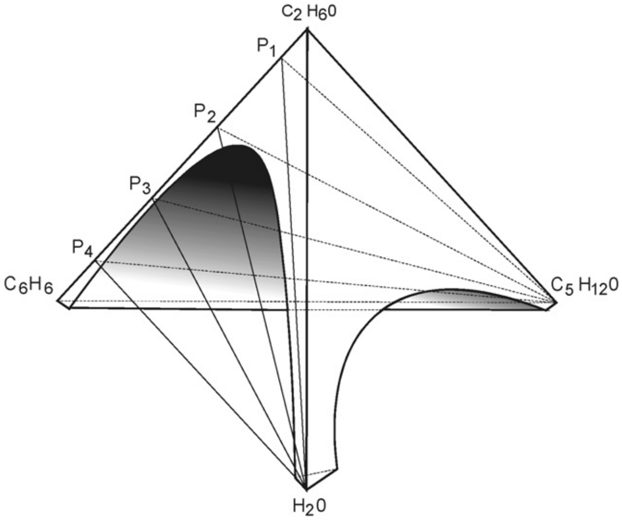

Fig. 1. Schematic representation of the [$w_1H_2O + w_2C_5H_{12}O + w_3C_2H_6O + w_4C_6H_6$] quaternary system at $T = 303.15$ K. P_1, P_2, P_3, and P_4 are sectional planes for the determination of the binodal surface.

A Mettler AG245 balance with an accuracy of ±0.00001 g was used to weigh the four components and the internal standard, in order to obtain a calibration curve for each component. To know which equation contained in the ChemStation soft provides the best fit for the experimental data in the calibration curves, we prepare several quaternary mixtures of well-known concentrations by mass. These mixtures were chromatographically analysed using each equation included in the software. These analyses show that the reported mass fraction values with the best fit equation have an uncertainty of ±0.001, while the detection limit was below a mass fraction of 0.0010, for water; 0.0015, for MTBE; 0.0037, for benzene; and 0.0031, for ethanol.

In order to determine the quaternary binodal surface, measurements were carried out at four different mixing ratios of ethanol and benzene, which characterize four quaternary planes (named P_1, P_2, P_3, and P_4 in Fig. 1). Fig. 1 shows a schematic representation of the quaternary system [$w_1H_2O + w_2C_5H_{12}O + w_3C_2H_6O + w_4C_6H_6$]. The equilibrium data for this system were obtained with the same procedure used for the ternary system. In this work, the initial mixtures (corresponding to the P_1, P_2, P_3, and P_4 planes) were selected to determine tie lines within the whole heterogeneous region.

3. Results and discussion

Table 1 lists the liquid–liquid equilibrium data for the ternary system [$w_1H_2O + w_2C_5H_{12}O + w_3)C_2H_6O$] at $T = 303.15 \pm 0.05$ K, which is classified as type 1 by Treybal,