J. Chem. Thermodynamics 41 (2009) 1279–1283

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Influence of temperature on the (liquid + liquid) equilibria of {3-methyl pentane + cyclopentane + methanol} ternary system at $T = (293.15, 297.15, \text{and } 299.15)$ K

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ARTICLE INFO

Article history:
Received 20 April 2009
Received in revised form 22 May 2009
Accepted 28 May 2009
Available online 6 June 2009

Keywords:
Data
(Liquid + liquid) equilibria
Ternary system
3-Methyl pentane
Cyclopentane
Methanol

ABSTRACT

In order to show the influence of temperature on the (liquid + liquid) equilibria (LLE) of the {3-methyl pentane (1) + cyclopentane (2) + methanol (3)} ternary system, equilibrium results at $T = (293.15, 297.15, \text{and } 299.15)$ K are reported. The effect of the temperature on the (liquid + liquid) equilibrium is determined and discussed. Experimental results show that this ternary system is completely homogeneous beyond $T = 300$ K. All chemicals were quantified by gas chromatography using a thermal conductivity detector. The tie line results were satisfactorily correlated by the Othmer and Tobias method, and the plait point coordinates for the three temperatures were estimated. Experimental values for the ternary system are compared with values calculated by the NRTL and UNIQUAC equations, and predicted by means of the UNIFAC group contribution method. It is found that the UNIQUAC and NRTL models provide similar good correlations of the solubility curve at these three temperatures. Finally, the UNIFAC model predicts binodal band type curves in the range of temperatures studied here, similar to those observed for systems classified by Treybal as type 2, instead of type 1 as experimentally observed. Distribution coefficients were also analysed through distribution curves.

1. Introduction

Studies of phase equilibria of systems constituted by mixtures of hydrocarbons with oxygenated compounds currently added to reformulated gasoline have gained interest in recent years in view of the production of lead free gasoline [1]. The US Environmental Protection Agency recommends the use of alcohols (methanol or ethanol) as gasoline additives to provide anti-knock properties and to help reduce harmful combustion emissions. In this work, (liquid + liquid) equilibrium data have been obtained for {3-methyl pentane (1) + cyclopentane (2) + methanol (3)} ternary system at $T = (293.15, 297.15, \text{and } 299.15)$ K with a constancy in temperature of ±0.05 K, in order to obtain the behaviour of blends of hydrocarbons and methanol at three temperatures. The equilibrium concentration for each component was determined by gas chromatography, using the internal standard method. Tie lines were also correlated using the Othmer and Tobias' method [2] and the plait point coordinates at each temperature are reported.

Furthermore, the experimental results were compared with those predicted by means of the UNIFAC group contribution method [3] using the LLE interaction parameters reported by Magnussen *et al.* [4], and correlated with the NRTL [5] and UNIQUAC [6] models fitted to those experimental results.

2. Experimental

2.1. Chemicals

All reagents were analytical grade. Methanol was from Merck, while 3-methyl pentane and cyclopentane were from Aldrich and Sigma, respectively. The purity of all reagents was checked using a HP 6890 gas chromatograph with a TCD detector coupled to a ChemStation and nitrogen as gas carrier, and was always better than 0.998 in mass fraction. Therefore, they were used without further purification.

2.2. Methods

Ternary mixtures of known overall composition within the heterogeneous region were prepared by mass, using several 16 cm^3 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 five 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, using the

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doi:10.1016/j.jct.2009.05.016

same methodology and experimental device previously reported [7]. 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 immediately placed in 2 cm^3 chromatographic vials, in order to be analysed by means of gas chromatography. For this purpose, the same chromatograph coupled to an Agilent 7683 autosampler was used. This autosampler was maintained at 1 K above of each work temperature in order to avoid phase separation during the time needed to make the chromatographic analysis. To obtain quantitative results, the same previously reported chromatographic method [8] was used.

In order to obtain a calibration curve for each component by the internal standard method, a Mettler AG245 dual range balance with an accuracy of ±0.1/0.01 mg was used to weigh the chemicals with the highest accuracy. Acetone (Merck, chromatographic quality) with a mass fraction purity >0.999 (GC) was used as the internal standard compound. On the other hand to obtain overall mixtures for LLE studies, we weighed the components with the lowest balance accuracy. For the three components, linear correlations always provided the best chromatographic fit for the calibration curves.

In order to obtain the uncertainty in the equilibrium mass fraction values, we prepared several ternary mixtures with very well known concentrations by mass. These mixtures were analysed with the chromatographic method and these results were compared with those obtained by mass. This comparison shows that the reported mass fraction values have an uncertainty of ±0.001.

Good separation of the four components was obtained with a similar method reported previously [7,8], but in this case keeping the oven at a constant temperature of 373 K for 5 min. Three or four analyses were performed for each sample in order to obtain a mean mass fraction value with repeatability better than 1%.

3. Results and discussion

3.1. Experimental

Experimental results for density, viscosity, and refractive index for the sodium D-line of pure compounds at $T = 298.15$ K are summarized in table 1. These properties were measured with a KEM DA-300 vibrating tube densimeter using degassed bi-distilled water and dry air as calibrating substances in accordance with the supplier instructions, an Anton Paar Stabinger viscometer (SVM 3000/G2) calibrated by the manufacturer, and a Leica AR600 refractometer, respectively. The densimeter and viscometer are equipped with their own Peltier effect control systems, which maintained the temperature of both apparatus at ± 0.01 K. A thermostatically water bath with a constancy of ±0.01 K was used for refractive index measurements. The uncertainties were $\pm 0.1\ \text{kg} \cdot \text{m}^{-3}$ for density, ±0.35% of the measured value for viscosity, and ±0.00005 for refractive index. For comparison, existing values found in the literature are also included in table 1.

Table 2 lists (liquid + liquid) equilibrium results, expressed in mass fraction, of (w_1 3-methyl pentane + w_2 cyclopentane + w_3 methanol) ternary system at $T = (293.15, 297.15, \text{and } 299.15)$ K with a constancy in temperature of ±0.05 K, while figure 1 shows the ternary equilibrium diagrams at the three temperatures, containing binodal curves and plait points (PP) calculated with the method of Othmer and Tobias. Experimental and correlated results at $T = 293.15$ K are shown in figure 2 for comparison. For the other temperatures, similar plots were obtained. Therefore, they were not shown.

Figure 1 shows that this ternary system is classified as type 1 in the Treybal's classification, because only one pair of partially miscible liquids is present [9]. Also, tie lines were satisfactorily correlated using the method of Othmer and Tobias method [2] that provides the plait point at each temperature.

Figure 3 shows a plot of the solubility of 3-methyl pentane in methanol at several temperatures reported in the literature [10] along with ours for comparison. As can be seen, a good concordance is obtained.

Since the concentrations of the three components were individually determined, the sums of the mass fractions for each phase in table 1 may slightly differ from unity (range ±0.001, in mass fraction). Material balances were performed for each tine line at each temperature in order to check the consistency of the equilibrium experimental values reported in table 2 [11]. These calculations show that our results satisfy the mass balance within an average absolute deviation of 1.53%, 0.92%, and 0.39% at (293.15, 297.15, and 299.15) K with a greatest deviation of 4.4%, 2.0%, and 0.4%, respectively.

3.2. Correlation

The LLE data were correlated with the UNIQUAC [6] and NRTL [5] equations, using an iterative computer program developed by Sørensen [12] that minimises the values of the following objective functions:

$$F_a = \sum^{k} \sum^{i} \left\{ \left(a_{ik}^{\mathrm{I}} - a_{ik}^{\mathrm{II}} \right) / \left(a_{ik}^{\mathrm{I}} + a_{ik}^{\mathrm{II}} \right) \right\}^2 + Q \sum^{n} P_n^2, \tag{1}$$

$$F_x = \sum^{k} \min \sum^{i} \sum^{j} (\mathrm{x}_{ijk} - \hat{x}_{ijk})^2 + Q \sum^{n} P_n^2, \tag{2}$$

TABLE 1

Density ρ, refractive index n_D, and viscosity η values of pure components at 298.15 K.

Chemicals	$\rho/(\text{kg} \cdot \text{m}^{-3})$		n_D		$\eta/(\text{mPa} \cdot \text{s})$	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Methanol	785.9	786.37[a] 786.45[b]	1.32650	1.32652[a] 1.32661[b]	0.542	0.542[b] 0.5513[a] 0.549[c]
3-Methyl pentane	658.8	659.76[a] 659.72[d]	1.37384	1.37386[a]	0.272	0.307[a] 0.306[c]
Cyclopentane	739.3	740.45[a] 739.92[e]	1.40341	1.40363[a]	0.408	0.416[a] 0.413[c]

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