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Isobaric vapor–liquid equilibrium for ternary mixtures of ethanol and methylcyclohexane with 3-methylpentane and *tert*-butyl alcohol at 101.3 kPa

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Abstract

Consistent vapor–liquid equilibrium (VLE) data for the ternary systems 3-methylpentane + ethanol + methylcyclohexane and ethanol + *tert*-butyl alcohol (TBA) + methylcyclohexane are reported at 101.3 kPa. The VLE data have been correlated by Wilson, UNIQUAC and NRTL equations. The ternary systems do not present azeotrope and are well predicted from binary interaction parameters.

Keywords: Vapor–liquid equilibria; Unleaded gasoline; Ethanol; *tert*-Butyl alcohol; Hydrocarbons

1. Introduction

This work presents a continuation on the thermodynamic research on vapor–liquid equilibrium (VLE) of mixtures formed by hydrocarbons and oxygenated additives (ethers and alkanols) to unleaded gasoline. Ethanol is used mostly because the availability of its feedstock from renewable resources. *tert*-Butyl alcohol (TBA) is added in the oxygenated gasoline with ethanol to avoid the formation of two liquid phases.

In this work, to improve our knowledge of the phase behaviour of alkanes with ethanol and *tert*-butyl alcohol mixtures, we measured isobaric VLE data at 101.3 kPa of the ternary systems 3-methylpentane + ethanol + methylcyclohexane and ethanol + *tert*-butyl alcohol (TBA) + methylcyclohexane. VLE data for constituent binary systems have been measured and reported previously [1–5]. The binary systems formed by an alcohol and a hydrocarbon (ethanol + 3-methylpentane [1], ethanol + methylcyclohexane [3] and TBA + methylcyclohexane [5]), deviate remarkably from ideality and present a minimum boiling temperature azeotrope. The binary system formed by the two hydrocarbons [2] shows a small positive deviation from ideality and does not present azeotrope. And the binary system formed by the two alcohols [4] exhibit negative deviation from ideal behaviour and does not present azeotrope. For these ternary systems, no VLE data have been previously published.

2. Experimental

2.1. Chemicals

3-Methylpentane (>99 mass%, *GC grade*), methylcyclohexane (>99 mass%, *anhydrous*), TBA (99.5 mass%, *HPLC grade*) were purchased from Aldrich Chemie Co., and ethanol (99.5 vol.%) was purchased from Prolabo. Alcohols were dried over molecular sieve type 4 Å as soon as the bottles were opened. The reagents were used without further purification after chromatography failed to show any significant impurities. The densities of pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are $\pm 0.01\ \mathrm{kg\,m^{-3}}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature.

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Table 1
Density, d, refractive index, n_D, and normal boiling point, T_b, of the chemicals

Component	d (298.15 K) (kg m^{-3})		n_D (298.15 K)		T_b (101.3 kPa) (K)	
	Experiment	Literature[a]	Experiment	Literature[a]	Experiment	Literature[b]
3-Methylpentane	659.62	659.80	1.3744	1.3739	336.30	336.43
Ethanol	785.04	785.01	1.3598	1.3594	351.41	351.48
Methylcyclohexane	764.92	765.00	1.4208	1.4206	373.96	374.10
TBA	775.40[c]	775.70[c]	1.3851	1.3851	355.33	355.56

[a] Ref. [13].
[b] Ref [10].
[c] Measured at 303.15 K.

2.2. Apparatus and procedure

An all-glass Fischer LABODEST vapor–liquid equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic recirculating still, equipped with a Cottrell circulation pump. The still is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Hart Scientific thermometer model 1502A and a Pt 1 0 0 probe Hart Scientific model 5622 calibrated at the Spanish *Instituto Nacional de Técnica Aeroespacial*. The accuracy is estimated to be ±0.05 K. For the pressure measurement, a digital manometer with an accuracy of ±0.01 kPa is used. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water.

In each VLE experiment, the pressure was fixed and held constant by using a vacuum pump, and the heating and shaking systems of the liquid mixture were turned on. The system was kept at the boiling point at least for 30 min to ensure that the steady state was reached. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed withdrawal of small volume samples (0.1 μL). At least two analyses were made for each sample.

2.3. Analysis

Concentration of the liquid and condensed phases were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d. capillary column DB-MTBE (J&W Scientific). The GC response peaks were treated with Chrom-Card for Windows, version 1.21. Column, injector and detector temperatures were 333, 473 and 498 K, respectively. Very good peak separation was achieved under these conditions and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. The standard deviation in the mole fraction was usually less than 0.001.

3. Results and discussion

The VLE data for the ternary systems are shown in Tables 2 and 3 and in Figs. 1 and 2. The activity coefficients γ_i were calculated assuming the non-ideality of both liquid and vapor phases from the following equation [6]:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + \frac{P}{2RT} \sum \sum y_i y_k (2\delta_{ji} - \delta_{jk}) \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^{L} the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, P_i^0 the pure-component vapor pressure and B_{ij} is the cross second virial coefficient and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. (1) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is

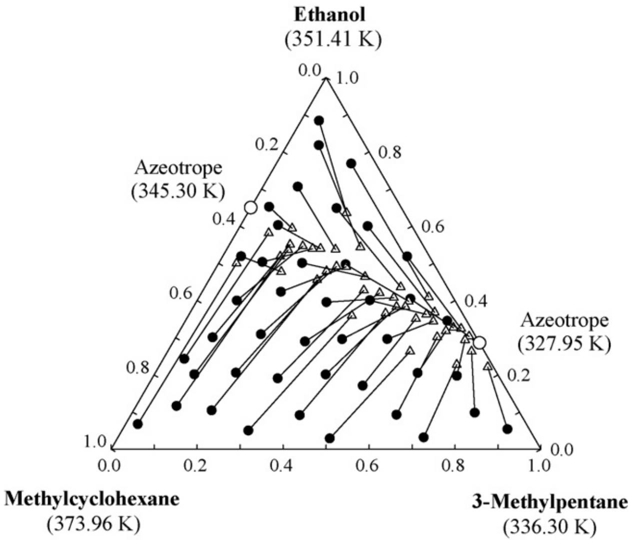

Fig. 1. Diagram of VLE for the ternary system 3-methylpentane (1) + ethanol (2) + methylcyclohexane (3) at 101.3 kPa: (●) liquid phase mole fractions; (△) vapor phase mole fractions; (○) azeotropes.