

Isobaric Vapour Liquid Equilibrium at 101.3 kPa for the Binary Mixtures 2-Methyl-2-Butene / Methanol and Isopentane / Methanol

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Due to the increased interest for using tertiary ethers as fuel additives (such as TAME – tert-amyl-methyl-ether synthesis), the research intensified to study its thermodynamic aspects. Mathematical modelling of tertiary ethers synthesis includes a number of elements characterizing the process thermodynamics. The liquid – vapour equilibrium data is used to get an insight about the deviations from ideal behaviour of the components in the two phases. This kind of information needed to characterize the process thermodynamics are widely available in literature, but sometimes with doubts related to accuracy, which leads to the necessity of experimental checking.

TAME is formed by reaction of isoamylenes present in FCC C₅-fraction (2-methyl-1-butene and 2-methyl-2-butene) with methanol (MeOH). The main inert compound present in the C₅-fraction is isopentane. The isobaric vapour-liquid equilibrium data (T-x-y) for the binary mixtures of methanol and 2-methyl-2-butene, methanol and isopentane are experimentally determined at 101.3 kPa.

The study performed gives a thorough determination of the whole binary system equilibrium data by means of a dynamic ebullometer Fisher 602 VLE. The analysis of both liquid and vapour phases were performed using a HP 5890 Series II Plus Gas Chromatograph with FID detector.

1. Introduction

Tert-amyl-methyl-ether (TAME) is the most widely used substitute of lead-based antiknocking additives in Europe. TAME is synthesized by reaction of the isoamylenes from C₅ fraction with methanol, e.g. Yamaki and Matsuda (2012). The present study deals with the vapour-liquid equilibrium of methanol with the isoamylenes present in a higher amount in the C₅ fraction, 2-methyl-2-butene, and of methanol with the main inert of the C₅ fraction, isopentane (Bonet-Ruiz, 2012). The design of reactive distillation technologies for TAME synthesis, such as the CDEtherol process, requires accurate knowledge about the activity coefficient, even at early design stages (Bonet-Ruiz et al, 2012). These equilibria are already available in the literature, but the equilibrium data determined is wider and more extensive than that found in literature, encompassing the whole curve. All experimental data has been fitted to several thermodynamic methods: Wilson, NRTL, UNIQUAC and VanLaar. Additionally, the experimental data obtained has been compared with data found in literature and predictions provided by the thermodynamic estimation methods UNIFAC, UNIFAC Dortmund (DDBST, 2013) and COSMO (COSMOlogic, 2013).

2. Material and method

All chemical compounds are supplied by Sigma-Aldrich with high purities: 2-methyl-2-butene (ref. 86262-250ML-F) purum, >= 95.0 %, Methanol (ref. 322415-2L) anhydrous, 99.8 % and Isopentane (ref. 59070-1L) puriss. p. a., >= 99.5 %. A commercial glass dynamic ebullometer apparatus type Labodest is used,

Fischer Model, D-53340 Type 0413-0120-00 Basic Unit. The analysis of the samples are performed in a gas phase chromatograph HP 5890 Series II equipped with flame ionisation detector (FID) and a capillary column Supelco (PTE-5 2-4159, 30 m x 0.52 mm internal diameter, 1 μm of phase thickness). Carrier gas is Helium and pressure control is electronic, integrated in the software ChemStation implemented on a computer linked to the chromatograph. A good chromatogram is obtained under the next operating conditions: 1 μL injected, constant oven temperature at No superpositions of the signal were detected and the peaks were well separated when using the following parameters: oven temperature at 90 $^{\circ}\text{C}$, Inlet A at 0.69 bar, channel C (hydrogen) at 1.03 bar, channel E (helium) at 1.22 bar.

3. Results and Discussion

3.1 2-methyl-2-butene / Methanol

The binary system methanol / 2-methyl-2-butene presents a non-ideal behaviour with the presence of a minimum boiling azeotrope at a molar composition around 0.78 2-methyl-2-butene and a temperature around 33 $^{\circ}\text{C}$ (Figure 1). It is interesting to notice that from a molar fraction of 2M2B from 0.2 to 0.9, the temperature of the corresponding vapour composition is close to the azeotropic composition. Although this behaviour is typical when there is liquid-liquid equilibrium, it was noticed experimentally that the mixture was totally miscible. Herrington (1951) thermodynamic consistency test is fulfilled with difference of $\sim 6.8\%$ between the areas.

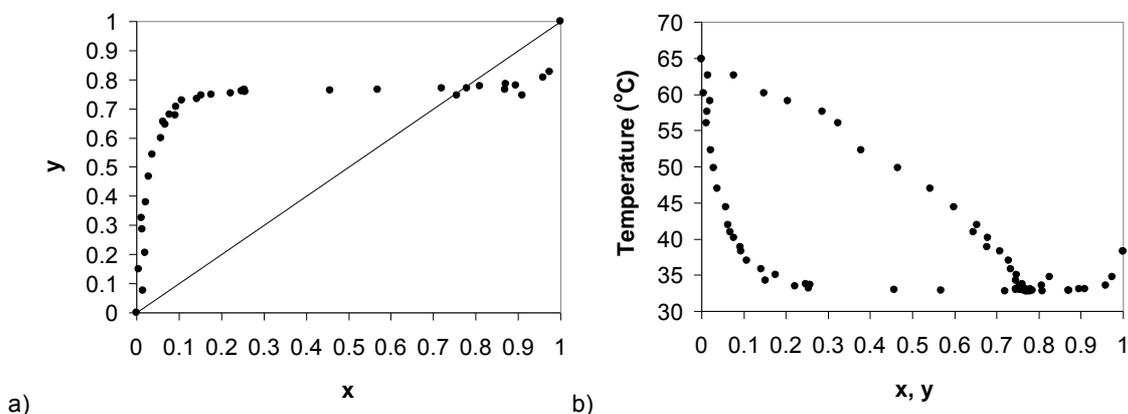


Figure 1: VLE 2-methyl-2-butene (1) / methanol (2), ($P = 1,013 \text{ mbar}$). a) x-y and b) T-x-y diagrams

The experimental results obtained are in accordance with the experimental results available from the literature (Figure 2). In the range of molar fractions 0.05 – 0.2 of 2M2B, the experimental values for the vapour phase mole fractions reported in literature are slightly lower, i.e. the liquid phase mole fraction 0.12 of 2M2B corresponds to a value of 0.66 - 0.67 vapour phase mole fraction 2M2B as reported by Rihko-Struckmann (2000), while in this work the value is 0.73. The azeotrope is identified to a 2M2B molar fraction between 0.78 and 0.79. When the temperatures are compared, they are very coincident, the liquid temperature reported by Rihko-Struckmann et al (2000) are about 0.5 $^{\circ}\text{C}$ over the rest but it is in the precision range. Figure 3 shows the adjustment of the experimental data to several thermodynamic models. Van Laar model provides the worst fitting as it does not take into account the influence of the temperature on the activity coefficients. The NRTL and UNIQUAC models provide the best correlations, being the recommended models for this binary mixture. The comparison of predictive models with the obtained experimental data is shown in Figure 4. The ab-initio model COSMO provides very good predictions, the main liquid temperature deviations of 5 $^{\circ}\text{C}$ and the position of the azeotrope is displaced 0.1 units. UNIFAC predicts a liquid-liquid equilibrium that does not exist. The prediction provided by the UNIFAC Dortmund does not indicate the liquid-liquid equilibrium, but the azeotropic composition is a bit higher than the experimental one, around 0.795, and the vapour compositions are slightly lower than the experimental ones. Nevertheless, as a prediction, the results are quite good for the UNIFAC Dortmund.

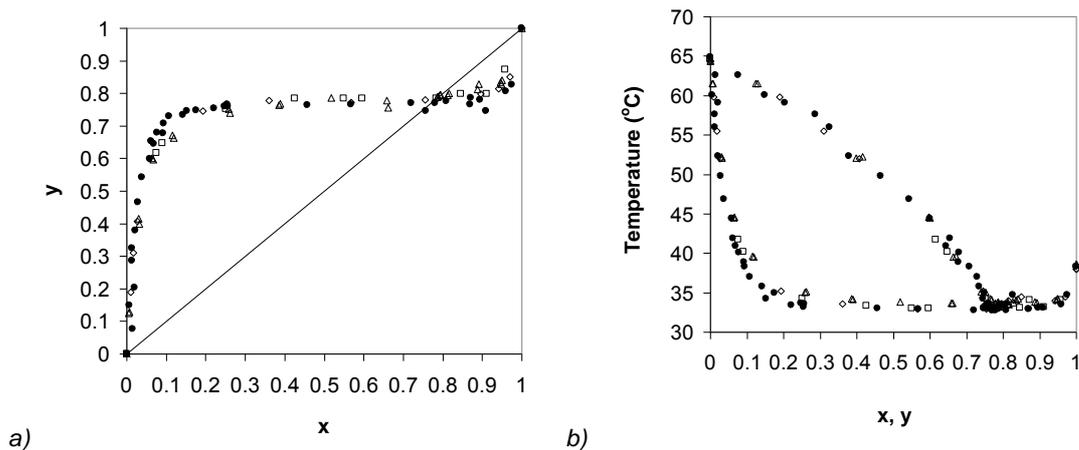


Figure 2: VLE 2-methyl-2-butene (1) / methanol (2), a) x-y and b) T-x-y diagram from data available in the literature ($P = 1,013$ mbar). \square Ogorodnikov et al (1960); \diamond Reichl et al (1998); \triangle Rihko-Struckmann et al (2000); \bullet this work

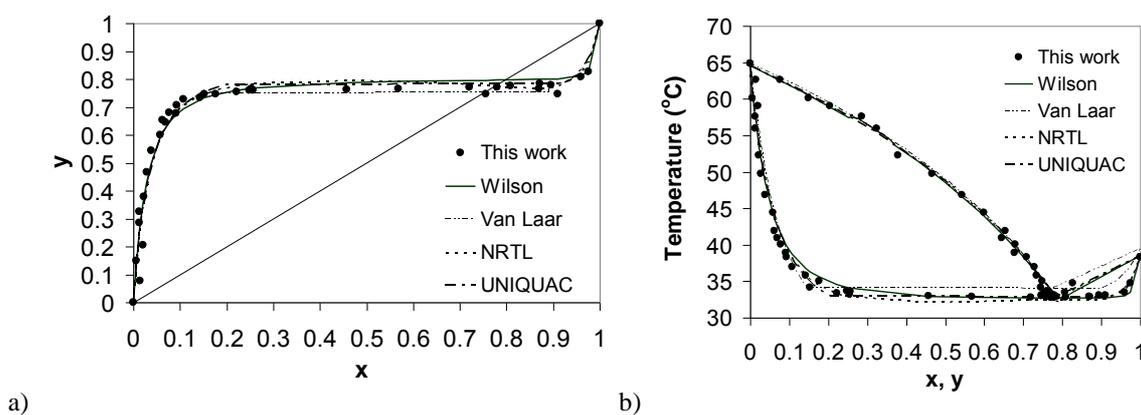


Figure 3: VLE 2-methyl-2-butene (1) / methanol (2), correlation of the experimental data to several thermodynamic models ($P = 1,013$ mbar). a) x-y and b) T-x-y diagrams

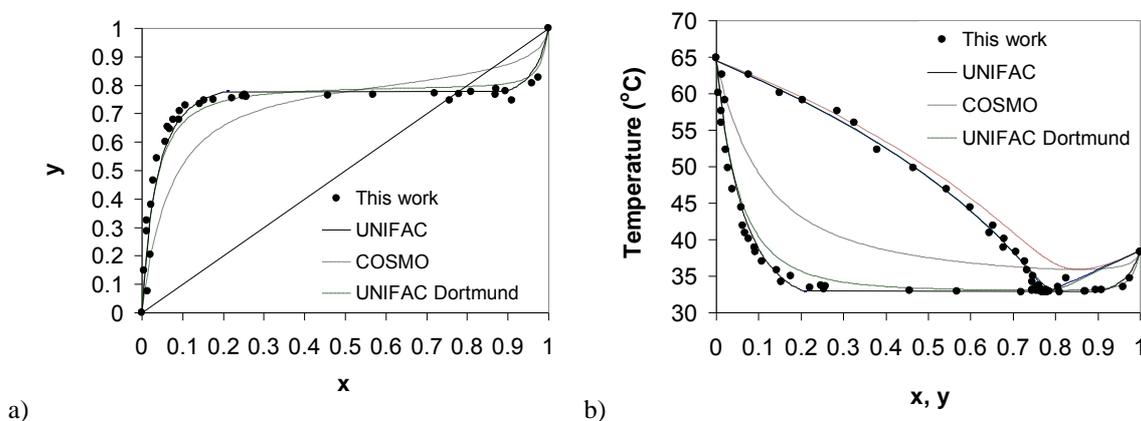


Figure 4: VLE 2-methyl-2-butene (1) / methanol (2), predictions compared with the experimental data ($P = 1,013$ mbar). a) x-y and b) T-x-y diagrams

3.2 Isopentane / Methanol

This experiment is focused on data for dilute solutions and near the azeotrope. The data follow a curve which suggests an easy separation because the vapour compositions are very far from the diagonal in the x-y diagram, however, a minimum boiling azeotrope is detected at 24 °C and isopentane molar fraction of 0.88 (Figure 5). The Herrington (1951) thermodynamic consistency test is fulfilled with difference of 0.35 % between the areas.

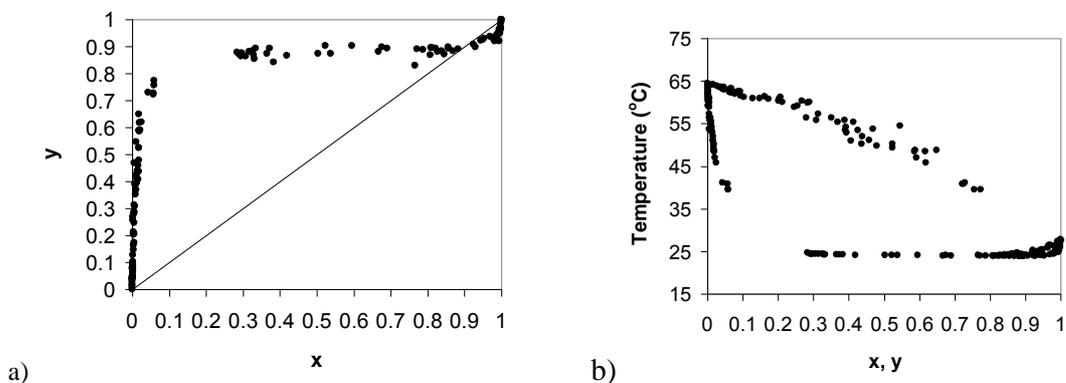


Figure 5: VLE isopentane (1) / methanol (2), ($P=1013$ mbar). a) x-y and b) T-x-y diagrams

The values found in literature fill the gap presented and are in a very good agreement with the experimental values obtained (Figure 6). Comparing with the literature data, the literature presents the azeotrope at 0.85 isopentane molar composition, a bit lower than 0.88 molar fraction. When representing graphically all the experimental data obtained by these authors, a rather small difference can be noticed in terms of position relative to the experimental points determined in this work, being closer to the lowest compositions. Although the difference is not important, the vapour compositions obtained are richer in volatile than the ones available in literature.

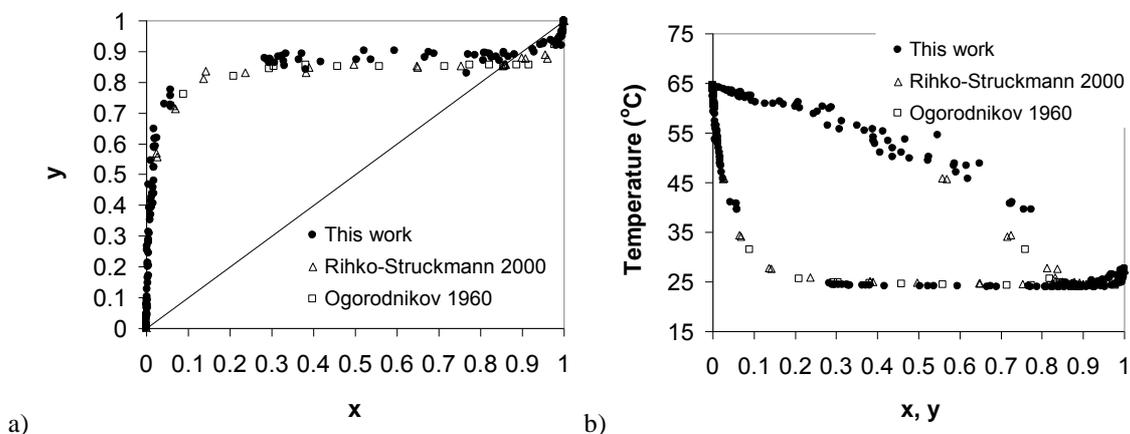


Figure 6: VLE isopentane (1) / methanol (2), data available in the literature ($P=1013$ mbar). □ Ogorodnikov et al (1960); Δ Rihko-Struckmann et al (2000); • this work. a) x-y and b) T-x-y diagrams

The experimental data are correlated to several thermodynamic models (Figure 7). The fitted parameters are given in Table 1. The worst correlation is depicted for the Van Laar model. UNIQUAC does not provide satisfactory results because it generates a liquid-liquid equilibrium which was not observed during the experimental work. NRTL fits without the liquid phase split, however, the best fitting is provided by Wilson thermodynamic method. The fitting is slightly improved if the non-ideal behaviour of isopentane in the vapour phase is taken into account instead of the ideal one. The Wilson fitting completed with an equation of state with Henry's law (HF) is also shown. The average temperature deviation and the root mean square error for the temperatures between the fitted and the experimental values is shown in Figure 9.

Comparing the experimental results with the estimation models, UNIFAC predicts a liquid-liquid equilibrium that does not exist experimentally (Figure 8). UNIFAC Dortmund provides the best prediction for mixtures rich in methanol and COSMO offers the best prediction in the range rich in isopentane.

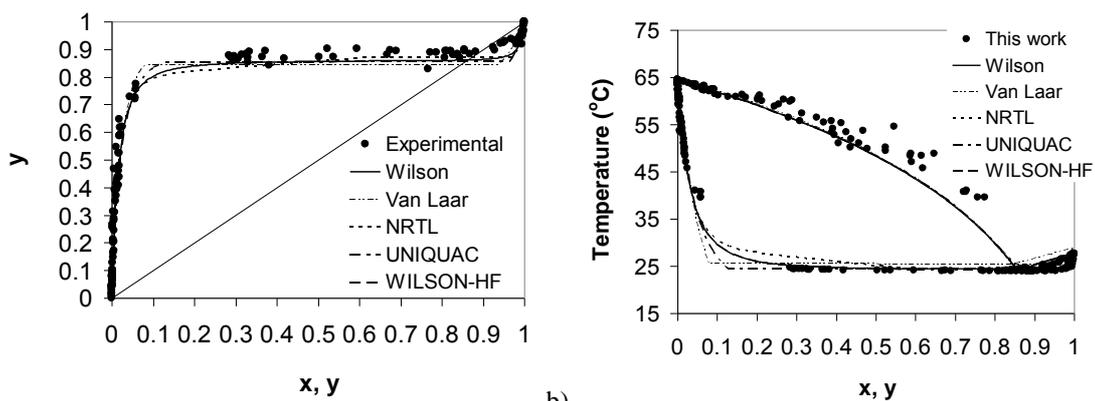


Figure 7: VLE isopentane (1) / methanol (2), correlation of the experimental data to several thermodynamic models ($P = 1,013$ mbar). a) x-y and b) T-x-y diagrams

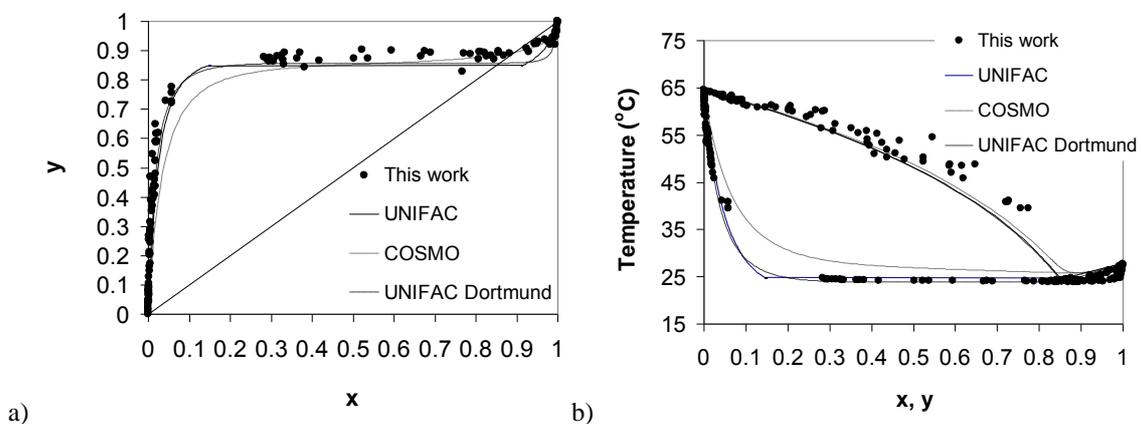


Figure 8: VLE isopentane (1) / methanol (2), predictions compared with the experimental data ($P = 1,013$ mbar). a) x-y and b) T-x-y diagrams.

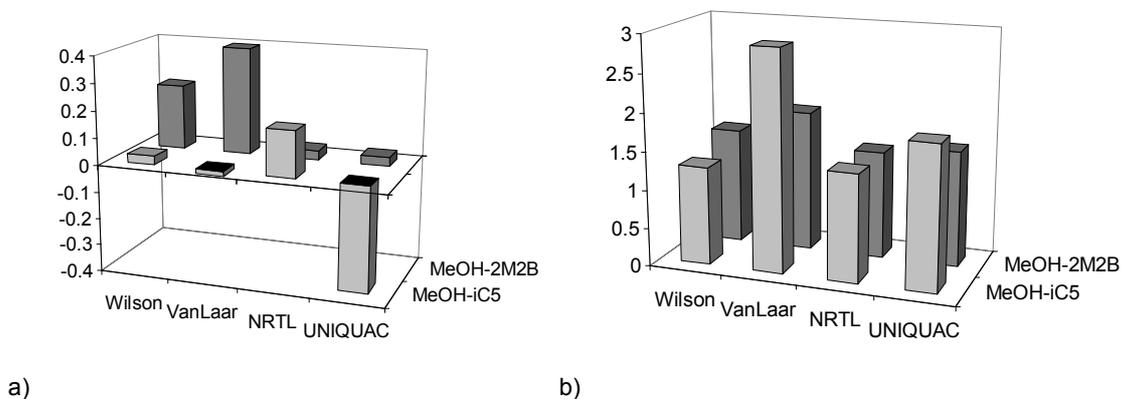


Figure 9: Thermodynamic model correlation for each binary system. a) Average temperature deviation, b) Root mean square error for the temperatures

Table 1: Estimated thermodynamic models parameters

		2M2B/MeOH	iC ₅ /MeOH
Van Laar	b_{ij}^{cma}	$7.491 \cdot 10^2$	$8.607 \cdot 10^2$
	b_{ji}^{cma}	$8.381 \cdot 10^2$	$9.290 \cdot 10^2$
	$\overline{\Delta T}$	0.3956	-0.0174
Wilson	b_{ij}^{cma}	$-5.043 \cdot 10^2$	$-6.063 \cdot 10^2$
	b_{ji}^{cma}	$-1.125 \cdot 10^3$	$-1.013 \cdot 10^3$
	$\overline{\Delta T}$	0.2401	0.0320
NRTL	b_{ij}^{cma}	$7.743 \cdot 10^2$	$9.817 \cdot 10^2$
	b_{ji}^{cma}	$4.868 \cdot 10^2$	$6.741 \cdot 10^2$
	$\overline{\Delta T}$	0.3974	0.4645
UNIQUAC	b_{ij}^{cma}	0.0345	0.1699
	b_{ji}^{cma}	$-7.615 \cdot 10^2$	$-8.479 \cdot 10^2$
	$\overline{\Delta T}$	5.716	-8.9354
		0.0329	-0.3896

4. Conclusions

Experiments were conducted in order to fully establish the equilibrium curves for methanol / 2-methyl-2-butene and isopentane / methanol. The experimental data is in good agreement with the available literature experimental data. The Herington thermodynamic consistency test is satisfied. Experimental data was fitted to several thermodynamic models being the best correlation using NRTL or Wilson. The predictions provided by UNIFAC Dortmund are quite accurate. The COSMO predictions are also quite satisfactory.

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