CHEMICAL ENGINEERING TRANSACTIONS

VOL. 35, 2013

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Varbanov, Jiří Klemeš, Panos Seferlis, Athanasios I. Papadopoulos, Spyros Voutetakis

ISBN 978-88-95608-26-6; **ISSN** 1974-9791

DOI: 10.3303/CET1335188

Isobaric Vapor Liquid Equilibrium at 101.3 kPa for the Binary Mixtures 2-Methyl-2-Butene / TAME and 2-Methyl-1-Butene / TAME

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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 from 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 C 5-fraction (2-methyl-1-butene and 2-methyl-2-butene) with methanol (MeOH).
The isobaric vapor liquid equilibrium data (T-x-y) for the binary mixtures of 2-methyl-2-butene and TAME, 2-methyl-1-butene and TAME 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 olefins of the c5 fraction with methanol, e.g. Yamaki and Matsuda (2012). The present study deals with the vapour liquid equilibrium of TAME with the main olefins present in the c5 fraction, 2-methyl-2-butene and 2-methyl-1-butene (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 equilibriums are already available in the literature, but the equilibrium data determined is wider and more extensive than that found in the 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 %, 2-methyl-1-butene (ref. 66035-50ML FLUKA) purum, >= 97.0 % and TAME (283096-500ML) 97 %. A commercial glass dynamic ebullometer apparatus typus labodest is used, Fischer Model, D-53340 Type 0413-0120-00 Basic Unit. The analysis of the samples are performed in a

Please cite this article as: Bernabeu Diaz M., Plesu V., Bonet Ruiz J., Bonet Ruiz A.E., Llorens Llacuna J., 2013, Isobaric vapor liquid equilibrium at 101.3 kpa for the binary mixtures 2-methyl-2-butene / tame and 2-methyl-1-butene / tame, Chemical Engineering Transactions, 35, 1129-1134 DOI:10.3303/CET1335188

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 ºC, 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 and TAME

The VLE data measured for the binary system 2M2B/TAME indicate a quite ideal behaviour (Figure 1). The volatility coefficient is around 6 but it is not totally ideal as the curve is not totally symmetric (Figure 2). Mixtures richer in 2M2B are slightly more distanced from the diagonal than the mixtures richer in TAME. The VLE experimental procedure is performed in two series, each one starting from pure components and following the curve up to the middle of the diagram. The coincidence of both half series in the middle also is an argument that the experiments are performed with good precision although the consistency test is not satisfied. The possible cause is that the vapour pressure of the pure TAME used for the consistency test is not in agreement with the experimental value.

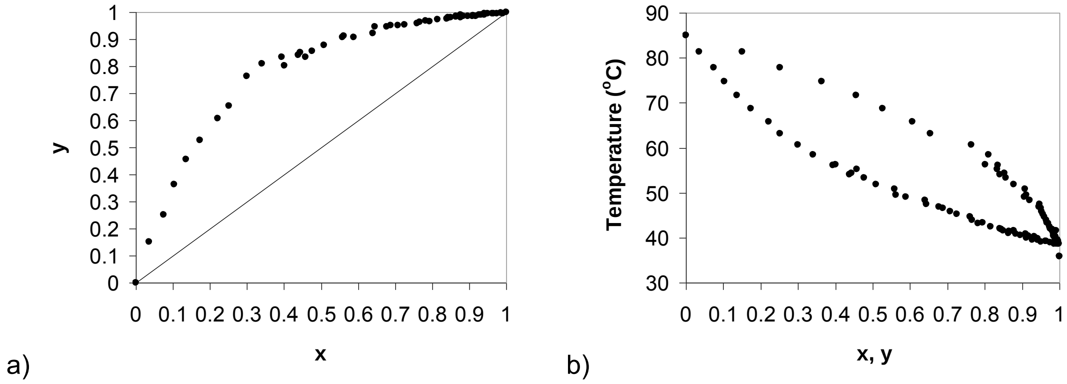


Figure 1:. VLE 2-methyl-2-butene (1) / TAME (2), (P=1013 mbar). a) x-y and b) T-x-y diagrams

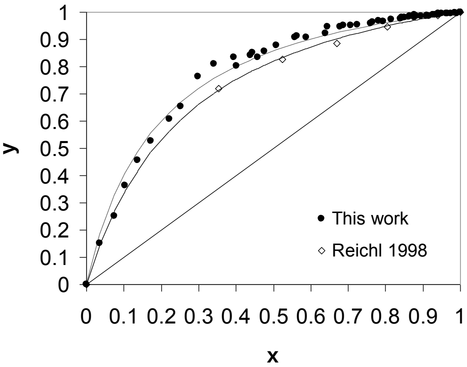
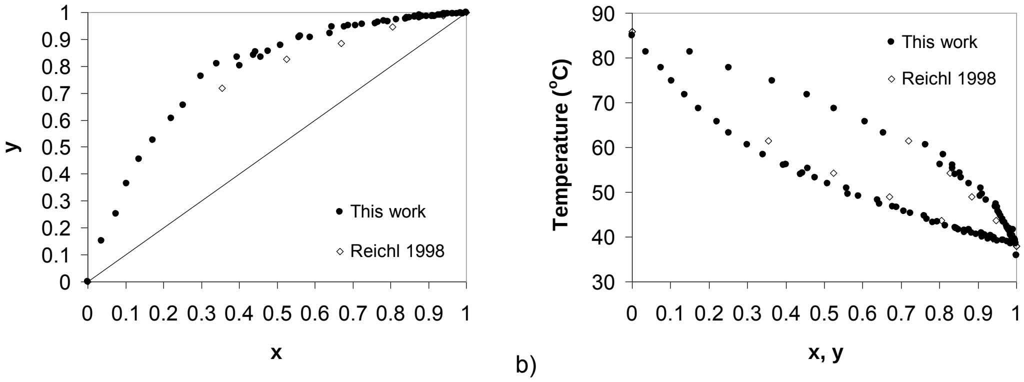


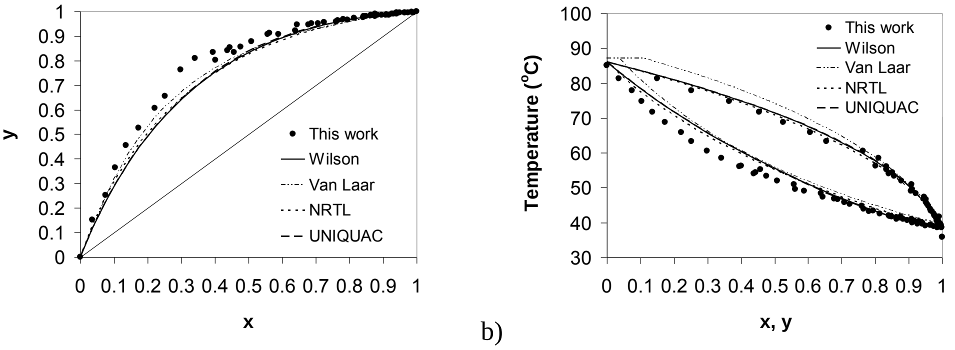
Figure 2:. VLE 2-methyl-2-butene (1) / TAME (2), correlation to a volatility coefficient for ideal mixtures (P=1013 mbar)

There are few experimental data available in the open literature related to this system, a possible reason being the difficulty to acquire the substances with a very high purity. The boiling point of pure TAME is around 86.3 °C and that of pure 2M2B is of 38.5 °C according to the Aspen Plus database. The experimental values obtained in this article are 85 °C for TAME and 35.9 °C for 2M2B. The boiling point of TAME obtained by Reichl et al (1998) is at 85.9 °C and of 2M2B is at 37.95 °C, which are closer to the boiling points of pure components. However, Reichl et al (1998) determined only 5 experimental points for this system (Figure 3). All experimental points determined by Reichl et al (1998) are obtained in the half graphic starting from pure 2M2B, but the other half graphic remained undetermined. If the system would be ideal the volatility coefficient for Reichl et al (1998) VLE data would be 4.56 (Figure 2). With exception of Van Laar, all the tested thermodynamic models to fit the experimental data provide a very similar quality of correlation. The correlations are not very satisfactory as the theoretical value line is always at the same side of the experimental points and not passing by the middle of them. The estimation methods evaluated provided very similar results (Figure 5), the ones of COSMO being between the results provided by UNIFAC and UNIFAC Dortmund. When the T-x-y diagram is observed, the UNIFAC provides a better correlation to experimental data for mixtures richer in TAME and the COSMO and UNIFAC Dortmund provide better correlation to experimental data for mixtures richer in 2M2B. The results of the predictions are closer to a more ideal behaviour of the mixture than the obtained experimental results. However the predicted x-y curves are always under the experimental data.



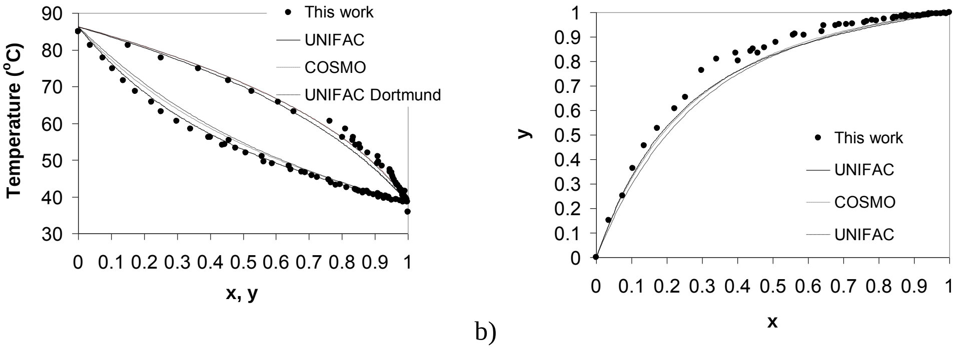
a) b)

Figure 3: VLE 2-methyl-2-butene (1) / TAME (2), diagram from data available in the literature (P=1013 mbar). a) x-y and b) T-x-y diagrams.



a) b)

Figure 4: VLE 2-methyl-2-butene (1) / TAME (2), correlation of the experimental data to several thermodynamic models (P=1013 mbar). a) x-y and b) T-x-y diagrams



a) b)

Figure 5: VLE 2-methyl-2-butene (1) / TAME (2), predictions compared with the experimental data (P=1013 mbar). a) xy and b) Txy diagrams

3.2 2-methyl-1-butene and TAME

The boiling temperature of TAME at 82.3 °C instead of the 85 °C as obtained in the previous experiment. The behaviour of this system is also quite ideal with a volatility coefficient of 7.6, but the VLE curve in the x-y diagram is not pointing to pure TAME corner (Figure 6). A possible TAME decomposition is affecting the concentrations near pure TAME vertex. However, there are not many available experimental data in literature for comparison. The experimental values obtained by Everson et al. (2001) can be correlated quite well to an ideal mixture with a volatility coefficient of 5.7 (Figure 7).

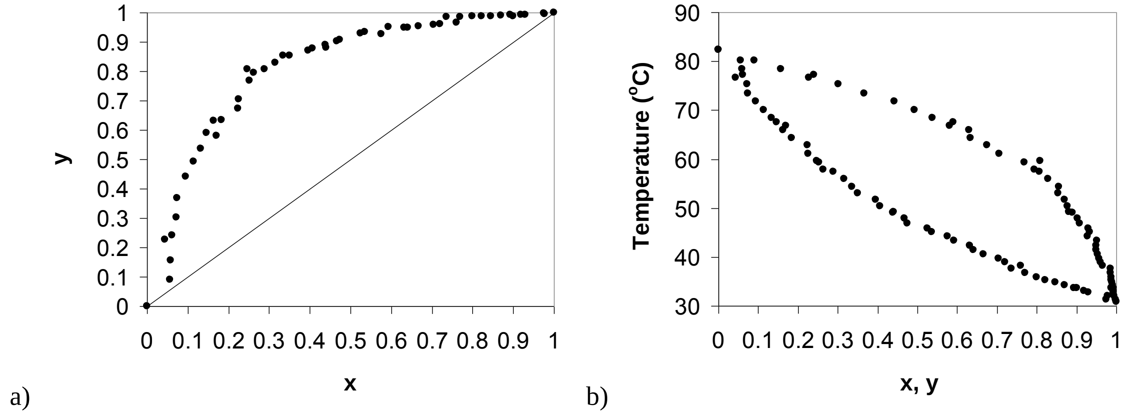


Figure 6. VLE 2-methyl-1-butene (1) / TAME (2), (P = 1,013 mbar). a) x-y and b) T-x-y diagrams

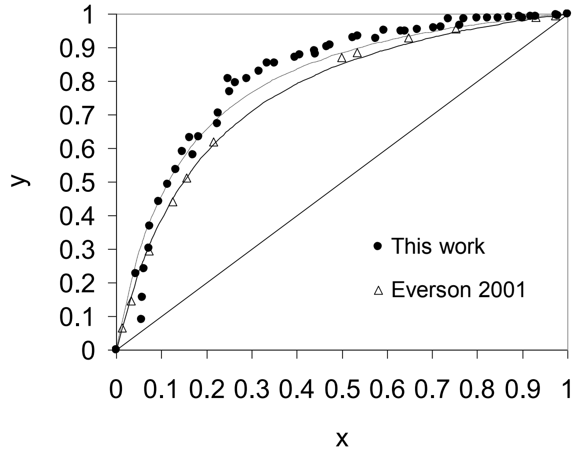
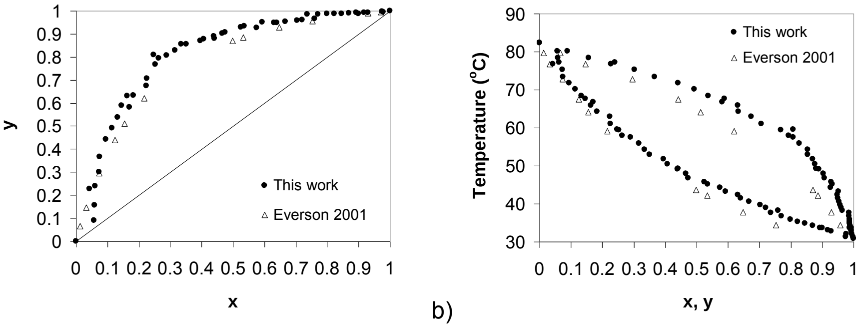


Figure 7:. VLE 2-methyl-1-butene (1) / TAME (2), correlation to a volatility coefficient for ideal mixtures (P = 1,013 mbar)

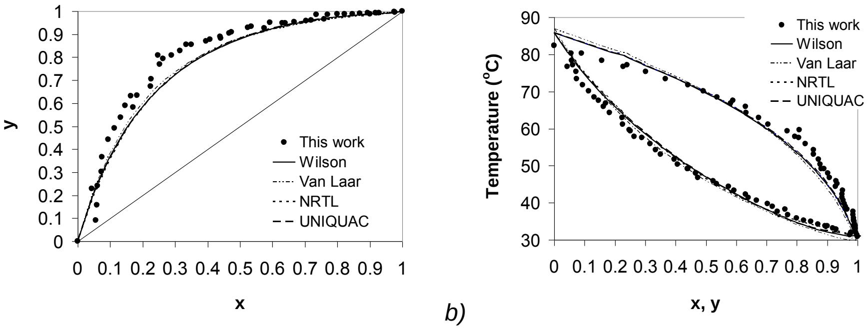
Everson et al. (2001) do not indicate the boiling temperature obtained for the pure substances (Figure 8). However, according to the tendency of the curves, it seems they reached quite low values in comparison with the pure component boiling point. As previously, when the data is correlated to thermodynamic models, all the models are very close to each other and closer to the x-y diagram diagonal (Figure 9). The average temperature deviation and the root mean square error for the temperatures between the fitted and the experimental values is shown in Figure 10. Predictive models are also closer to the diagonal (Figure 11). The predictions of COSMO are between the predictions using UNIFAC and UNIFAC Dortmund, although all of them are very close to each other. The fitted parameters are given in Table 1.

The study of these binaries is particularly significant since the experimental results suggest that the glass material of the dynamic ebullometer may act as catalyst provoking TAME decomposition. This fact can be concluded also from the failure of the thermodynamic consistency tests performed for these binary mixtures. The data available in literature for these binary systems is very scarce but it shows a good agreement with the own experimental data. However, a more thorough experimental data processing is required in order to accurately characterize the real behaviour of these mixtures



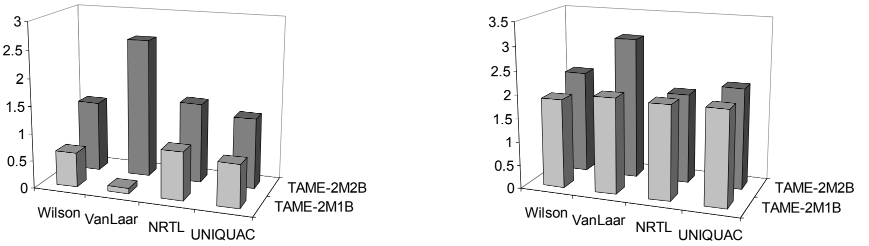
a) b)

Figure 8: VLE 2-methyl-1-butene (1) / TAME (2), from data available in the literature (P = 1013 mbar). a) x-y and b) T-x-y diagrams



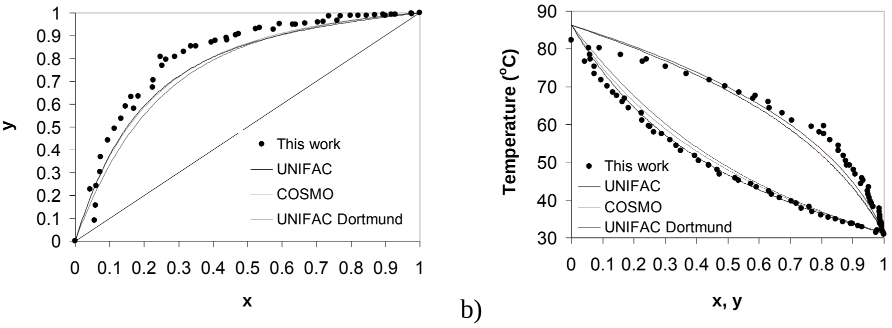
a) *b)*

Figure 9: VLE 2-methyl-1-butene (1) / TAME (2), correlation of the experimental data to several thermodynamic models (P=1013 mbar). a) x-y and b) T-x-y diagrams



a) b)

Figure 10: Thermodynamic model correlation for each binary system. a) Average temperature deviation, b) Root mean square error for the temperatures



a) b)

Figure 11: VLE 2-methyl-1-butene (1) / TAME (2), predictions compared with the experimental data (P=1,013 mbar). a) x-y and b) T-x-y diagrams

Table 1: Estimated thermodynamic models parameters.

		2M2B/TAME	2M1B/TAME
Van Laar	b_{ij}^{cma}	10^4	$4.011\cdot 10^1$
	b_{ji}^{cma}	$-3.799\cdot 10^1$	10^4
	$\overline{\Delta T}$	2.5396	0.1049
Wilson	b_{ij}^{cma}	$3.949\cdot 10^2$	$3.611\cdot 10^2$
	b_{ji}^{cma}	$-1.012\cdot 10^3$	$-2.721\cdot 10^3$
	$\overline{\Delta T}$	1.2983	0.6334
NRTL	b_{ij}^{cma}	$-3.310\cdot 10^2$	$8.766\cdot 10^2$
	b_{ji}^{cma}	$4.575\cdot 10^2$	$-4.543\cdot 10^2$
	$\overline{\Delta T}$	0.358038	0.3000
UNIQUAC	b_{ij}^{cma}	1,4595	0.8867
	b_{ji}^{cma}	$-4.719\cdot 10^2$	$-5.519\cdot 10^2$
	$\overline{\Delta T}$	$2.769\cdot 10^2$	$2.810\cdot 10^2$
		1.2845	0.7791

4. Conclusions

Experiments were conducted to establish the full equilibrium curve for 2-methyl-2-butene / TAME and 2-methyl-1-butene / TAME. The Herrington thermodynamic consistency test (Herrington, 1951) was applied to the obtained experimental data and was not satisfied on both systems. Although, there is experimental data available in the literature, further experiments are required to check the vapour pressure of pure TAME and its possible decomposition. Experimental data is fitted to several thermodynamic models, such as Van Laar, Wilson, UNIQUAC and NRTL. The worst fitting was provided by the Van Laar model while the other models provided a similar, but not optimal, fitting. Additionally, the experimental data was compared to that provided by estimation methods, such as UNIFAC, UNIFAC Dortmund and COSMO. COSMO provided a middle point between both versions of UNIFAC while UNIFAC Dortmund provided the estimations closer to the experimental points in both systems.

Acknowledgements

The authors would like to thank the financial support National University Research Council, grant TD-188/2007 and the project CTQ2009-11465 (Ministry of Science and Innovation – Spanish Government) who provided the opportunity to complete this research.

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