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VAPOUR LIQUID EQUILIBRIUM MEASUREMENTS FOR PROCESS DESIGN

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Helsinki University of Technology
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ABSTRACT

In recent years it has become increasingly important to develop new oxygenate and isooctane technologies and processes that meet the continuously stricter environmental requirements. Some of the new process schemes use renewable raw materials in order to meet the European Union biofuel requirements. One of the most important requirements for the design of such separation processes includes the knowledge of vapour liquid equilibrium (VLE) behaviour. There are methods to estimate VLE but for the final design and with new systems VLE needs to be determined experimentally. Unfortunately, the existing equipment used for the VLE measurements suffer from labour intensiveness. The application of automation to VLE measurement apparatuses provides increasing accuracy and speed, thus reducing the cost for VLE measurements. In the present work three different apparatuses were developed. Using the constructed apparatuses, VLE was measured for relevant systems in the modelling and design of oxygenate and isooctane technologies.

Firstly, a static apparatus for VLE measurements was built, which allowed the analysis of samples from the liquid and vapour phases, by means of an automated sampling system. Measurements were made on ethanenitrile + 2-methylpropane and ethanenitrile + 2-methylpropene systems. No VLE measurements were not found in the current literature for the systems measured with the static apparatus in this work. The systems measured disclosed a positive deviation from Raoult's law. In addition, azeotropic behaviour was observed for the ethanenitrile + 2-methylpropane system.

Secondly, a circulation still was made. The still was used to obtain isobaric and isothermal VLE data for nine alkane + alcohol and alkene + alcohol binary systems. An on-line system with circulation of the samples was tested with two analysis methods, mass spectrometry and gas chromatography. The on-line system was then applied to the ethanol + 2,4,4-trimethyl-1-pentene and 2-propanol + 2,4,4-trimethyl-1-pentene systems at atmospheric pressure and vapour pressure was determined for 2-methoxy-2,4,4-trimethylpentane. VLE measurements were made for the methanol + 2-methoxy-2,4,4-trimethylpentane system. Again, no VLE measurements were found in existing for most of the systems measured with the recirculation still. The results exhibited positive deviation from Raoult's law. All the systems measured exhibited azeotropic behaviour, with the exception of the methanol + 2-methoxy-2,4,4-trimethylpentane system.

Thirdly, a static total pressure apparatus was constructed. With the manual version of the apparatus 12 binary systems consisting of alkanes + 2-butanol and alkenes + alcohols were measured. The static total pressure apparatus was upgraded to one of a computer-controlled

level, which requires substantially less labour than the manual version of the apparatus. Using the computer-controlled version, measurements were made for five binary systems consisting of 2-methylpropene + alcohols. Most of the measurements made with the static total pressure apparatus were for systems for which measurements have not been available earlier. The systems measured exhibited positive deviation from Raoult's law and some of the systems exhibited azeotropic behaviour.

The gamma-phi approach was used for modelling the systems measured. The vapour phase was calculated with the Soave modification of the Redlich-Kwong-equation and the Wilson activity coefficient model was used for modelling the liquid phase behaviour. Legendre-polynomials were used in the Barker's method for the data reduction of the static total pressure measurements. In addition to the Wilson equation parameters, NRTL and UNIQUAC activity coefficient model parameters were also determined for the C4-alkene + alcohol systems measured with the static total pressure apparatus. The Wilson equation provided the best fit of the measurements, compared to NRTL and UNIQUAC models. The Antoine-equation was used for describing the vapour pressures of the pure components with the exception of the static total pressure measurements, for which the actual measured vapour pressure values were used.

PREFACE

The thesis is based on work accomplished at Fortum Oy Pilot Hall in Kilpilahti and at Helsinki University of Technology, Laboratory of Chemical Engineering and Plant Design between 1998 and 2003.

Both supervisors, Professor Simo Liukkonen and Professor Juhani Aittamaa, deserve special mention for providing the guidance needed.

Colleagues Juha-Pekka Pokki, Younghun Kim, Marko Laakkonen, Tuomas Ouni, Raimo Ketola and Virpi Tarkiainen contributed ideas and their expertise.

Ismo Viitala, Bjarne Bremer, Merja Teittinen and many other former colleagues at the Pilot Hall have my deepest gratitude for advice in building the apparatus described in the first article. Kari Keskinen provided valuable support and encouragement by reading and offering comments on the manuscript of the first publication.

Several professionals at the mechanical and electrical workshop of the university contributed to this work: technicians Pekka Koivulaakso, Heikki Viianranta, Heikki Wilkman (now retired) and the glass blower Kalevi Karppinen turned ideas into reality.

Finally, humble thanks to my wife Heli and daughters Heta and Hilppa for their constant support and understanding.

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Petri Uusi-Kyyny

LIST OF PUBLICATIONS

This thesis includes the papers listed below. The papers are referred to in the text by their Roman numerals.

I. Uusi-Kyyny, P. and Liukkonen, S., Vapor Liquid Equilibrium for the Binary Systems of 2-Methylpropane + Ethanenitrile and 2-Methylpropene + Ethanenitrile at 358 K, *J. Chem.Eng. Data* **45** (2000) 116-119.

II. Uusi-Kyyny, P., Pokki, J.-P., Aittamaa, J. and Liukkonen, S., Vapor Liquid Equilibrium for the Binary Systems of 2-Methyl-2-propanol + 2,4,4-Trimethyl-1-pentene at 333 K and 348 K and 2-Butanol + 2,4,4-Trimethyl-1-pentene at 360 K, *J. Chem.Eng Data* **46** (2001) 686-691.

III. Uusi-Kyyny, P., Pokki, J.-P., Aittamaa, J. and Liukkonen, S., Vapor-Liquid Equilibrium for the Binary Systems of 3-Methylpentane + 2-Methyl-2-propanol at 331 K and + 2-Butanol at 331 K, *J. Chem.Eng. Data* **46** (2001) 754-758.

IV. Uusi-Kyyny, P., Pokki, J.-P., Aittamaa, J. and Liukkonen, S., Vapor-Liquid Equilibrium for the Binary Systems of Methanol +2,4,4-Trimethyl-1-pentene at 331 K and 101 kPa and Methanol +2-Methoxy-2,4,4-trimethylpentane at 333 K, *J. Chem. Eng. Data* **46** (2001) 1244-1248.

V. Pokki, J.-P., Uusi-Kyyny, P., Aittamaa, J. and Liukkonen, S., Vapor-Liquid Equilibrium for the 2-Methylpentane + 2-Methyl-2-propanol and + 2-Butanol at 329 K, *J. Chem. Eng. Data* **47** (2002) 371-375.

VI. Uusi-Kyyny, P., Pokki, J.-P., Laakkonen, M., Aittamaa, J. and Liukkonen, S., Vapour liquid equilibrium for the binary systems 2-methylpentane + 2-butanol at 329.2 K and n-hexane + 2-butanol at 329.2 and 393.2 K with a static apparatus, *Fluid Phase Equilib.* **201** (2002) 343-358.

VII. Uusi-Kyyny, P., Tarkiainen, V., Kim, Y., Ketola, R.A. and Aittamaa, J., Vapor Liquid Equilibrium for the Binary Systems of Ethanol+2,4,4-Trimethyl-1-pentene at 101 kPa and 2-propanol+2,4,4-Trimethyl-1-pentene at 101 kPa, *J. Chem. Eng. Data* **48** (2003) 280-285.

VIII. Laakkonen, M., Pokki, J.-P., Uusi-Kyyny, P. and Aittamaa, J., Vapour Liquid Equilibrium for the 1-Butene + Methanol, + Ethanol, + 2-Propanol, + 2-Butanol and + 2-Methyl-2-Propanol Systems at 326 K, *Fluid Phase Equilib.* **206** (2003) 237-252.

IX. Pokki, J.-P., Laakkonen, M., Uusi-Kyyny, P. and Aittamaa, J., Vapour Liquid Equilibrium for the cis-2-Butene + Methanol, + Ethanol, + 2-Propanol, + 2-Butanol and + 2-Methyl-2-Propanol Systems at 337 K, *Fluid Phase Equilib.* **212** (2003) 129-141.

X. Ouni, T., Uusi-Kyyny, P., Pokki, J.-P., Aittamaa, J., Isothermal Vapor Liquid Equilibrium for Binary 2-Methylpropene + Methanol to Butanol Systems, *J. Chem. Eng. Data* **49** (2004) 787-794.

STATEMENT OF THE AUTHOR'S ROLE IN LISTED PUBLICATIONS

Petri Uusi-Kyyny's (PUK) contribution to the appended publications:

I PUK designed and set up the sampling system, conducted the experimental work and prepared the manuscript.

II PUK acquired the knowledge to build this apparatus and assembled it. The test runs were made together with the co-author Juha-Pekka Pokki. PUK prepared the manuscript, took part in the experimental work and trained the technical staff.

III and IV PUK prepared the manuscript and trained the technical staff in the operating procedures of the apparatus.

V PUK participated in the interpretation of the results.

VI The experimental set-up was designed by PUK. PUK supervised the construction and assembly of the apparatus and the degassing system. The paper was primarily prepared by PUK.

VII The experimental work was done in cooperation with The Technical Research Centre of Finland (VTT). The sampling system was designed with the co-authors. The manuscript was prepared by PUK, in cooperation with the co-authors.

VIII & IX PUK participated in the preparation of the manuscript and the interpretation of the results.

X PUK conducted part of the experimental work, tutored the author of the paper in the experimental technique and participated in the examination of the results.

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INTRODUCTION

Processes used for producing chemicals require separation operations, of which one of the most widely used is distillation. In distillation the separation of components is achieved by formation of vapour and liquid phases. The phases often have different compositions, which allow the enrichment of the components. Accurate vapour liquid equilibrium (VLE) data is therefore a cornerstone of reliable process design in the chemical industries. The design of new chemical processes must constantly be carried out in order to be in the vanguard of continuous cut-throat economic competition. The intensification of process development attempts to cut down the time consumed from the first laboratory experiment to the start-up of the new process through extensive use of mathematical modelling. Using mathematical models minimises the need for experimental work in several development phases (laboratory, bench, pilot and demonstration unit scales). The last experimental phases of process development are the most expensive and time-consuming. For successful modelling, accurate physical properties must be provided at conditions of practical interest [1], [2]. Lacking or inadequate knowledge of the physical properties can severely reduce the accuracy of process simulations [3]. The designing of separation processes requires a knowledge of the behaviour of vapour liquid equilibrium, which is also frequently used in reactor design.

Estimation methods have proven to be valuable tools for the chemical engineer in the preliminary stage of design, but there is still a need for VLE measurements, especially for non-ideal systems. For the final design, accurate information based on experiments is essential, due to the considerable capital investment of the chemical production facilities. Further development of estimation methods, however requires more VLE data to be published.

Values of the physical properties in a process can vary greatly from component to component. Because the type and construction of the apparatuses used in VLE measurements are determined by the physical properties of the components in the systems to be measured, different apparatus types are needed for them. In this work, three apparatuses were set up for the measurement of vapour liquid equilibrium. The apparatuses built were used to obtain VLE measurements that are used in the design of new processes.

The focus of industrial importance in research can change due to environmental legislation and political decisions: 2-methoxy-2-methylpropane (MTBE) and later other oxygenates were introduced to the gasoline pool in the 80s and 90s in order to prevent smog in the big cities [4] and to eliminate the use of lead compounds. In the beginning of the 21st century, MTBE was banned on 31st December, 2003 due to environmental concerns in California [5], New York and

Connecticut, and it will possibly be banned in the whole USA [6]. This necessitates changes in the gasoline supply and is therefore reflected in the processes used to produce the fuel.

The development in Europe is different: ethers in gasoline are not banned. Biofuels will be favoured in order to meet the demands of the Kyoto agreement. Large production facilities of bio-ethanol make the production of 2-methoxy-2-methylpropane (ETBE) possible through fiscal incentives. The European ETBE production started in the early 90s and currently reaches 500,000 ton/a. In Europe, the demand for fuel oxygenates is currently stable at approximately 3.5 million ton/a, the majority of which (3 million ton/a) is still met by MTBE [7].

COMPONENTS OF INTEREST

1.1 2-Methylpropene

2-Methylpropene is used as a feed in all of the processes associated with this work. Catalysts are used to enable the reactions of 2-methylpropene. In most cases, an acid ion-exchange resin catalyst is used for the etherification of 2-methylpropene with methanol or ethanol to produce 2-methoxy-2-methylbutane (MTBE) or 2-ethoxy-2-methylbutane (ETBE).

The 2-methylpropene feed is most often introduced from the Fluid Catalytic Cracking (FCC) unit. Other sources of 2-methylpropene are the steam-cracking process in the production of ethylene and propylene and 2-methyl-2-propanol dehydration [8]. 2-Methylpropane from field butanes is also dehydrogenated into 2-methylpropene [9].

The 2-methylpropene feed stream from the FCC unit contains other C4-alkenes, C4-alkanes and C4-alkynes. Because the C4 stream frequently contains impurities that poison the ion-exchange resin catalyst, the C4 stream is washed with water to lower the ethanenitrile content the most harmful catalyst poison to below 1 ppm [10]. When the C4 feed contains less than 1 ppm of ethanenitrile, the typical useful age of the catalyst bed varies from 2 to 5 years. When the feed contains more than 1 ppm ethanenitrile, the useful age of the catalyst is reduced significantly. With an increase in the ethanenitrile content however, the useful age of the catalyst is reduced significantly. The accumulation of the ethanenitrile in the circulation streams enhances the deactivation of the etherification catalyst.

1.2 2-Methoxy-2-methylbutane

2-Methoxy-2-methylbutane (MTBE) is manufactured from methanol, bought on the market, and 2-methylpropene in the presence of an acid catalyst, which most often is an ion-exchange resin. The most important side reactions are the dimerisation of 2-methylpropene (when there is too small an amount of methanol), methanol condensation to dimethylether (when the methanol amount is too large) and, in the presence of water, the reaction of the 2-methylpropene with water to 2-methyl-2-propanol. As the temperature and the residence time increase, more side-reaction products are formed in the MTBE process [11].

Modelling the behaviour of ethanenitrile in the processes utilizing the C4 stream from the FCC unit requires reliable vapour liquid equilibrium measurements [1]. This model can be used to find a cost-effective solution for ethanenitrile removal from the process; for example, by preventing the

ethanenitrile from entering the reactor, an increase in the effective lifespan of the catalyst in the etherification and dimerisation reactors can be found.

Vapour liquid equilibrium measurements for methanol + C4-alkene systems are not readily available. In the literature to date, the methanol + 2-methylpropene system at 40 °C [12] as well as one excess enthalpy measurement for this system exist [13]. For the other alkene systems no VLE measurements could be found in the literature, thus necessitating the determination of the VLE for the methanol + C4-alkene systems. [VIII]-[X].

On the other hand, extensive studies have been published for the methanol + n-butane system [14], including excess-enthalpy measurements [13], [15]. There are also VLE measurements available for the methanol + 2-methylpropane system in the existing publications [16].

Although VLE measurements were not found in the literature for binary systems of ethanenitrile + 2-methylpropene and + 2-methylpropane, they were available for other ethanenitrile + C4-alkanes and -alkenes [I]. One conclusion drawn from the extant studies is that the binary systems of ethanenitrile + C4-hydrocarbons are non-ideal and exhibit large positive deviations from Raoult's law, the methanol + C4-hydrocarbon systems also exhibit similar behaviour.

1.3 2-Ethoxy-2-methylbutane

In the 2-ethoxy-2-methylbutane (ETBE) processes the alcohol used in the etherification is changed from methanol, used in the MTBE processes, to ethanol. Ethanol produced by the fermentation of agricultural products is considered an environmentally friendly, renewable energy source. The use of ethanol in gasoline has been promoted by tax subventions both in Europe and in the USA. In Europe most of the ethanol is etherified [7] whereas in the USA, ethanol is blended as such into the gasoline because ETBE is an ether similar compared to MTBE, which polluted the ground waters in the Santa Barbara area, due to leakages in fuel tanks of petrol stations. The drawback of the direct ethanol blending is the difficulty it presents in meeting the gasoline vapour pressure regulations [17]. The vapour pressure regulations are compromised because ethanol and the hydrocarbons used in motor gasoline form mixtures with positive deviations from Raoult's law, so that mixing ethanol into gasoline containing hydrocarbons and ethers raises the vapour pressure [18]. Tertiary ethers like MTBE, ETBE, TAAE and TAME form ideal mixtures with hydrocarbons, thus adding tertiary ethers to gasoline lowers the vapour pressure of the gasoline [19].

In ETBE processes, the composition and control of the azeotropic point plays a significant role [20]. Although VLE have been published for C4-alkanes with ethanol [14], [21], the amount of published data is scarce for C4-alkenes + ethanol systems. Some measurements provide, for example, only 6 points per isotherm, thus making it difficult to obtain the hydrocarbon + ethanol azeotropic composition accurately [22]. There are also binary pairs for which measurements were not publicly available at all, for example 1-butene+ethanol. Measurements with the static total pressure apparatus were therefore made to determine the behaviour of the various C4-alkenes with ethanol [VIII]-[X].

1.4 2,2,4-Trimethylpentane

On the one hand, the upcoming MTBE ban in California initiated vigorous activity to find a substitute in sufficient quantity for MTBE. On the other hand, there are engineers running MTBE plants looking for an economical way to produce some fuel component other than MTBE that would require the fewest possible changes in the production facilities.

Applying a side reaction of the MTBE process, the dimerisation of 2-methylpropene, was considered, though this requires a second step, the hydrogenation of the 2,4,4-trimethylpentenes (diisobutylene) to a high-quality sulfur-free fuel component, isooctane, in order to meet the gasoline maximum olefin contents regulations. For the reaction necessary to produce diisobutylene, however any further oligomerisation reaction must be inhibited. This can be achieved with polar components, where one option is to use 2-methyl-2-propanol which is formed from 2-methylpropene reacting with water [23].

In the 2-methylpropene dimerisation process, the most important VLE behaviour was determined to be the hydrocarbon + alcohol systems. The behaviours of hydrocarbons + alcohol mixtures are non-ideal and for the alkenes + alcohol systems VLE measurements could not be found in any existing literature. Although some references were found for the C6-alkane + alcohol system, new measurements were made to increase the reliability of the VLE model of the 2-methylpropene dimerization process [II], [III], [V]. Furthermore VLE had to be determined for the 2,4,4-trimethyl-1-pentene + alcohol systems and C6-alkane + alcohol systems [III]-[VII]. The systems exhibited positive deviations from Raoult's law and azeotropy. The system behaviour is needed not only for the design of the separation system, but also in the kinetic modelling of the reaction.

Reducing the time needed for this number of VLE experiments is essential not only for cost savings but also because it has to be possible to provide crucial data for process design on

demand. One solution to this problem is available in the form of the static total pressure method [24], [VI], [VIII]-[X].

1.5 2-Methoxy-2,4,4-trimethylpentane

The higher molecular weight ethers can be attractive gasoline components due to the fact that the water solubility of the ethers with higher molecular weight is smaller than that of ethers with lower molecular weight, the octane ratings are high [25] and their vapour pressures are low. Because vapour pressure measurements for the 2-methoxy-2,4,4-trimethylpentane and vapour liquid equilibrium measurements for the components involved in the etherification of trimethylpentenes with methanol were not previously available, the vapour pressure measurements and VLE measurements had to be determined [IV].

THERMODYNAMIC MODELS

The proper selection of thermodynamic models is the starting point for successful use of the measured VLE in process simulation. Measurements made in the course of this work allow the simulation of processes, which can be assumed to operate at sub-critical temperatures and pressures thereby permitting the use of an activity coefficient model for the modelling of the liquid phase. The Wilson equation [26] was most often used for the presentation of the liquid phase behaviour due to the fact that it most frequently provides the best presentation of alcohol+(C4-C18) hydrocarbon and alcohol + alcohol systems, compared to other activity coefficient models [27]. For the C4-hydrocarbon + alcohol systems also the NRTL [28] and UNIQUAC [29] equation parameters were regressed. From personal experience gathered in regressing alcohol + hydrocarbon systems, the Wilson equation proven to be the most suitable for representing these systems [VII], [IX], [X]. In addition, the presentation of multi-component behaviour is possible with the binary parameters. It is however assumed that no liquid-liquid phase split is to be modelled in these systems at the temperature and composition range of interest. Legendre-polynomials were used in Barker's method [30] for the data reduction of the static total pressure measurements [VI].

The Soave modification of the Redlich-Kwong equation with quadratic mixing rules was used for the calculation of the vapour phase [31] and binary interaction parameter k_{ij} in the attractive term was set to the value of zero. Using binary interaction parameters for the calculation of the vapour phase, fugacity coefficient in the so-called gamma-phi approach did not contribute to a more precise description of the systems studied.

The Antoine equation was used for describing the vapour pressures of pure components of the measurements [II]-[V].

The thermodynamic consistency of the measured data can be investigated, if the equilibrium vapour phase and the liquid phase compositions are analysed and the temperature and pressure of the system are measured. The integral test [32], the point test [32] and the infinite dilution test [33] were used for checking the consistency of the measurements. Unfortunately, consistency testing is not possible for the measurements made with the static total pressure method.

APPARATUS FOR VAPOUR LIQUID EQUILIBRIUM MEASUREMENT

1.6 Introduction

VLE measurements are tedious and time-consuming [34] as measurement conditions are often controlled and recorded manually. Cost reduction can be achieved by affordable automation, which permits a more efficient operation of the apparatus and, in some cases, an increase in accuracy. One problem associated with automation is that researchers working with experimental thermodynamics seldom seem to have the expertise needed in laboratory automation. When, however automation expertise has been successfully created in the laboratory, the goal should be to implement data acquisition programs and automation software to increase the measurement output of the experimental devices. It is thereby possible to decrease the cost of one individual measurement point substantially [35].

Suitable methods for determination of VLE vary. In some cases several methods can be applied, but in the most difficult cases measurements are almost impossible. The selection of methods and apparatuses depend on the physical properties of the system studied: vapour pressure, component stability, material compatibility, measurement accuracy and safety. The properties determined specifically for binary vapour liquid equilibrium systems are temperature, pressure and the compositions of the constituent phases.

1.6.1 Temperature measurement

For temperature measurements in the range of 0 to 100 °C, platinum resistance -thermometer probes are favoured. For temperatures above 150 °C, thermocouples are often used [36]. Advice on high-accuracy temperature measurements is available at the National Centre for Metrology and Accreditation. This organisation also provides important calibration services.

1.6.2 Pressure measurement

Temperature compensated pressure transducers are the most frequently used device for pressure measurement in VLE determination, but Bourdon pressure gauges have also been used [36]. Dead-weight piston gauges are mostly used for calibration purposes only. The cost of the pressure transducer depends on two things: its accuracy and temperature compensation. It is usually difficult to find pressure transducers, which are thermally compensated for temperatures above 373 K and with an accuracy of better than 0.1 % of full scale of the pressure measurement device. In addition, the fluids studied in the experiments may be corrosive, which decreases the possible number of candidates for the pressure measurement device. If there is no need for pressure transducer temperature compensation, the cost of pressure measurement is lowered.

This is the case when using dynamic equilibrium stills. Furthermore, when measuring the pressure it is essential to ensure the reliability of the measurements by correct and regular calibration.

1.6.3 Composition determination

The determination of composition is the most complex task: the devices needed are often expensive and there is no universal analytical device that is suitable for all components. Gas chromatography is used most often for the determination of the composition of phases. Other methods for composition determination, although seldom applied in VLE measurements, include mass spectrometry, various spectroscopic methods, and density and refractive measurement.

1.7 Dynamic equilibrium stills

In the dynamic equilibrium stills the mixture is brought to boil under controlled pressure. The vapour and liquid mixture is separated in the equilibrium chamber and the vapour phase is condensed and returned to the boiling chamber. The liquid phase formed in the equilibrium chamber is also circulated. The composition of the boiling liquid and the vapour change with time until a steady state is achieved [37]. In a properly working the steady state represents still the true equilibrium values or, in other words, one equilibrium step. The principle of a dynamic equilibrium still is presented in Figure 1.

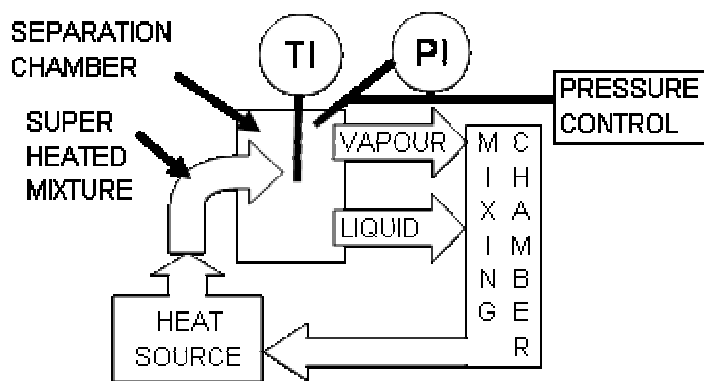


Figure 1. The principle of a dynamic equilibrium still.

The development of the dynamic still type apparatus can be considered to have reached the mature stage of progress [38]. The investment cost is small if a glass blower is resident. The instrumentation can be purchased from a multitude of companies and assembling the apparatus is fast and easy. With these kinds of apparatuses it is possible to begin the experimental work quickly. The automation of these apparatuses also demands the automation of the sampling system, which can be achieved by circulating the samples [VII]. Pressure-regulation systems are commercially available at a reasonable price. With these apparatuses conditions are favourable

for measuring one total composition at several pressures, analysing the vapour and liquid samples. Adding and removing the components to change the total composition in the still are most easily done manually. One challenge that should be mentioned in the use of the automated apparatus is the possible need to adjust the heat input to the Cottrell pump.

1.8 Static VLE apparatus

In the static method, the degassed components are fed to the equilibrium cell. The volume of the cell can either be controlled or uncontrolled. The temperature and pressure are regulated to assure that two phases are present. The runs carried out with this type of apparatus are most often isothermal. The content of the cell is agitated in order to shorten the equilibration time. Samples are drawn from the liquid and vapour phases and analysed, for example, with gas chromatography or mass spectrometry. These samples can also be drawn from sample circulation lines. The principles of the static method are presented in Figure 2. The challenging task is to ensure that the samples analysed represent the equilibrium state. The problems that arise are associated with the partial condensation of the vapour phase and the partial vaporisation of the liquid phase, during sampling and sample transfer. Another drawback of this type of apparatus is the time needed for producing one isotherm and the calibration of the analyser. An advantage is that the results obtained can be tested with consistency tests.

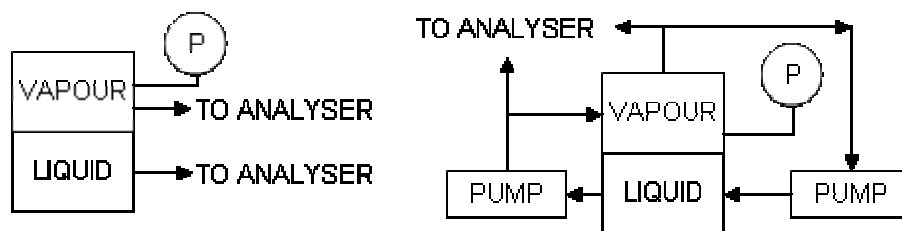


Figure 2. The principles of a static VLE measurement apparatuses.

1.9 Static total pressure method

In the static total pressure method, the analysis of the samples of the constituent phases is avoided. The total composition in the equilibrium cell is determined either by weighting the cell or by injecting precise volumes of the components into the cell. The measurements are isothermal and the equilibrium pressure is measured. The amount of components in the liquid phase and the vapour phase is calculated iteratively [VI]. The static total pressure method is a fast and efficient method for determining VLE for binary mixtures with the additional advantage that the apparatus using the static total pressure method has been successfully computer-controlled [39].

The drawbacks are: the method cannot be used for reactive mixtures, degassing of the components is required, consistency checking of the results is not possible and data from ternary vapour liquid-liquid-equilibrium VLLE measurement are difficult to interpret [40].

1.10 Flow through apparatus

The principle of the flow-through method is presented in Figure 3. In the flow-through method the system is open and two or more components are pumped in a constant flow into the cell until a steady state is reached. The vapour and liquid phases are then analysed. This method is suitable for temperature-sensitive and reactive components [41]. The amount of mixture can be high which makes the analysis of the samples easier, but for expensive components this is not a favourable feature [42]. In some experimental set-ups, it is difficult to control the vapour liquid interface level in the cell as well as the component flow rates. Sometimes there are difficulties in obtaining representative samples.

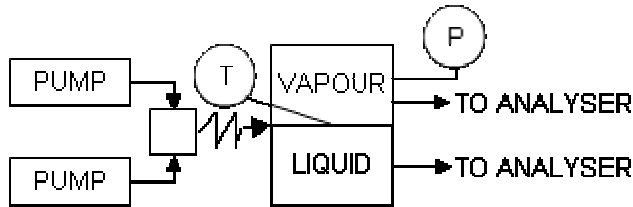


Figure 3. The principle of a flow-through apparatus.

1.11 Dew and bubble point measurement apparatus

In the dew and bubble point method, the measurements usually consist of pressure, volume, temperature and constant cell composition, as depicted in Figure 4. The dew and bubble point pressures are determined from the pressure-volume behaviour at constant temperature. The advantage of this method is the elimination of the need for the sampling and analysis. The correction required in the total pressure measurements is not needed in this method, the densities of mixture can be measured and the critical point can also be determined. One of the drawbacks is the difficulty in the observation of the dew point. The components used have to be carefully degassed [43]. Furthermore, the time needed for the determination of one isotherm is appreciably longer than when using the static total pressure method.

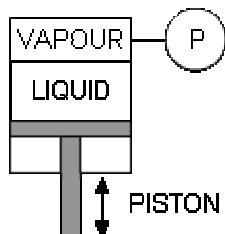


Figure 4. The principle of dew and bubble point measurement method.

APPARATUSES CONSTRUCTED FOR THIS WORK

The motivation for this work came from the industrial need of VLE data and the fact that the experimental information for most of the systems measured was not available in open sources. The apparatuses built were tailored for the VLE determination of C4-hydrocarbon + alcohol, C4-hydrocarbon + ethanenitrile systems and C5-C8 hydrocarbon + alcohol systems.

The apparatus type used in the measurements is determined by the following factors:

1. Availability
2. Feasibility for the systems studied: materials, temperature and pressure range and safety issues
3. The accuracy needed
4. Cost
5. Time needed for the measurements
6. Level of expertise needed by technical staff and human resources

VLE measurement devices actually built enable the measurements in the temperature and pressure ranges presented in Figure 5.

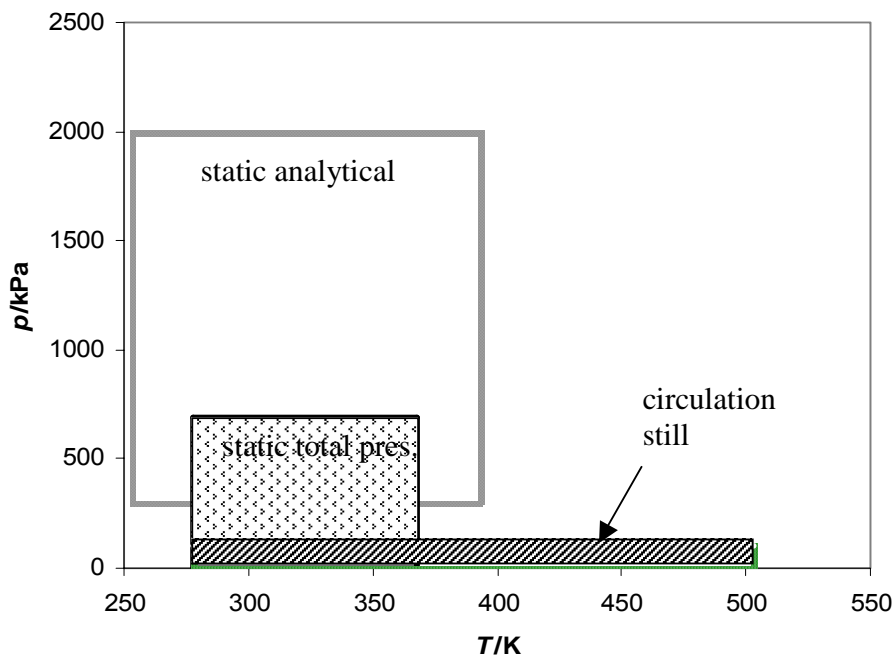


Figure 5. Temperature and pressure range of the apparatus built.

1.12 Static apparatus with sampling

For the measurements in this work, the flow-through type method was discarded for the following reasons: voracious consumption of materials, the accuracy can be worse than with the static total pressure method and mixtures studied were non-reacting. The dew and bubble point measurement method was discarded as well because it is not possible to use consistency tests to evaluate the measurements made.

A commercial DB Robinson JEFRI sapphire cell apparatus for the determination of bubble points and critical temperatures was available for use so the decision to build the static method type with circulation of the liquid phase for sampling and with the withdrawal of vapour samples from the equilibrium cell. The sampling system was automated and controlled by means of the gas chromatograph (GC) software. The advantage of this method is the elimination of manual manipulation to withdraw samples for sample bombs and transfer to the GC, thus saving time and increasing accuracy. Also repetitive samples can be analysed without disturbing the equilibrium. The analysis of both the vapour and liquid phase permit consistency testing of the measurements. The drawbacks of the chosen system were the time needed for producing one measurement point (2 h) and the high pressure of the system (>300 kPa) needed in order to get a reliable vapour sample. If the system measured contains a liquid-liquid phase split at lower temperatures near the system temperature studied, then there is a danger of erroneous liquid composition values. This danger is due to the phase split in the sample transfer line. The sample transfer line must be traced but the temperature of the line cannot be raised above the system temperature due to the formation of vapour liquid split.

The accuracy of the pressure measurement was ± 9 kPa and the accuracy of the temperature measurement was ± 0.06 K. The success of the composition determination of the phases in equilibrium is largely determined by the accuracy of the GC calibration. The accuracy of the composition determination for the 2-methylpropene + ethanenitrile system is, on average, better than ± 0.004 in mole fraction and for the 2-methylpropane + ethanenitrile system better than ± 0.013 in mole fraction. Even though a solvent was used to prevent the formation of a phase split at room temperature the GC-calibration accuracy decreased for the 2-methylpropane + ethanenitrile system.

The measurements presented in [1] were evaluated with the integral test as well as the point test for thermodynamic consistency, passing the criteria for both tests. The pressure residuals were larger than the experimental uncertainty for the 2-methylpropane + ethanenitrile system, which is probably due to errors in the analysis of the components and caused by the possible formation of the liquid-liquid split. For the 2-methylpropene + ethanenitrile system the pressure residuals are

within the experimental uncertainty. Azeotropic behaviour was observed for the 2-methylpropane + ethanenitrile but for the 2-methylpropene + ethanenitrile system it was not detected.

1.13 Circulation still

The circulation still was built to study the behaviour of alcohols+alkanes and +alkenes interactions. The building, setup and testing progressed quickly because of earlier experience with the same type of apparatus [44]. The volume of the mixture needed for VLE measurements or the volume of the pure component used for vapour pressure determination was approximately 80 cm³. Minimising the amount of material needed for running the apparatus is important if the chemicals used are expensive or toxic; also the amount of waste, which has to be disposed of after the experiments, is smaller. The uncertainty in the temperature measurement was ± 0.05 K (Frontek, Thermolyzer, S2541) and ± 0.07 K (Ametek, DT-100 [VII]) and the pressure measurement accuracy was ± 0.15 kPa. Composition determination accuracy ranged from ± 0.002 to ± 0.004 in mole fraction. The azeotropic compositions are presented for the 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene system in figure 6. The azeotropic compositions from [II], [45] and [46] are well in line with one another. Estimations made with the UNIFAC-Dortmund modification differ from the measured ones approximately between 0.02 and 0.03 in mole fraction.

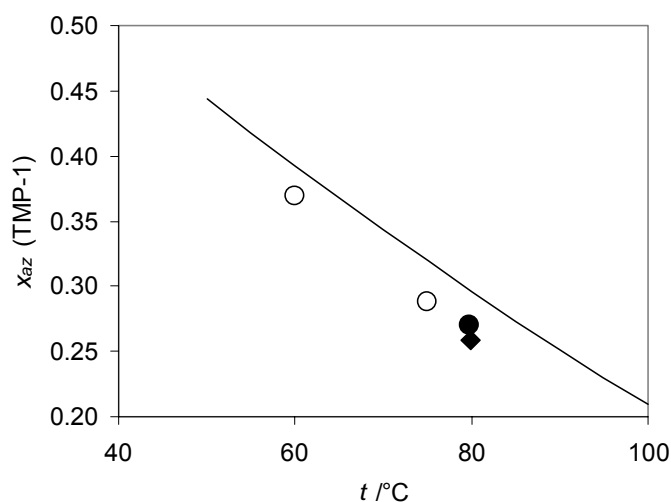


Figure 6. Azeotropic compositions for the 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene (TMP-1) system \circ [II], \bullet [45], \blacklozenge [46], — UNIFAC Dortmund modification [47].

The measurements presented in [II] for the 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene and 2-butanol + 2,4,4-trimethyl-1-pentene systems passed the integral test. The infinite dilution test plots revealed that the datasets measured were not consistent in the dilute range. The inconsistencies of the measurements were probably due to incomplete mixing of the liquid and

condensed vapour phase in the sampling chambers and in the mixing chamber. The systems measured passed the point test, with the exception of the 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene at 333 K. Azeotropic behaviour was observed for all systems measured.

The mixing of the liquid and condensed vapour phase in the sampling chambers and in the mixing chamber was improved for the measurements presented in [III]-[V], [VII]. The measurements for the 3-methylpentane + 2-methyl-2-propanol system at 331 K and 3-methylpentane + 2-butanol system at 331 K were tested by means of the integral test, point test and the infinite dilution test [III]. The measurements made for the 3-methylpentane + 2-methyl-2-propanol system passed the three consistency tests. The 3-methylpentane + 2-butanol system passed the integral test and the point test, but failed the infinite dilution test. The improvement of the mixing setup enabled us to conduct runs in which measurements of high quality were produced, even though the infinite dilution test was not passed for the 3-methylpentane + 2-butanol system. Azeotropic behaviour was observed for all systems measured.

In addition to the alcohol + alkane, +alkene systems, measurements were made which can be used in the design of 2-methoxy-2,4,4-trimethylpentane processes. The vapour pressure measurements for the 2-methoxy-2,4,4-trimethylpentane and some VLE measurements were performed with the circulation still [IV]. One density point was also measured for 2-methoxy-2,4,4-trimethylpentane [IV]. Later Verevkin et al. [48] published vapour pressure measurements for the same component applying a different method and found that the vaporisation enthalpies calculated from their measurements compared to measurements in the experiments performed for this thesis [IV] were consistent with each other. In the methanol + 2-methoxy-2,4,4-trimethylpentane system the still successfully worked at relative volatilities less than 40. The measurements satisfied the integral test, the point test and the infinite dilution test criterions. Whereas the methanol + 2,4,4-trimethyl-1-pentene system measured exhibited azeotropic behaviour, it was not detected for the methanol + 2-methoxy-2,4,4-trimethylpentane system. The measurements made satisfied the integral test, the point test and the infinite dilution test criterions.

VLE was measured for the 2-methylpentane + 2-methyl-2-propanol system at 329 K and 2-methylpentane + 2-butanol system at 329 K [VI]. The measurements satisfied the integral test, the point test and the infinite dilution test criterions. Azeotropic behaviour was observed for the systems measured.

An on-line analysis system was devised and tested [VII]. The on-line analysis of the constituent vapour and liquid phases is tempting since the equilibration time can be minimised, thereby making the measurement procedure more efficient. The circulation of the samples with pumps is

possible if both phases are circulated continuously, which assures that the total composition of the circulating mixture does not change. By circulating either the liquid phase or the condensed vapour phase the total composition of the mixture circulating in the still changes. The composition change is due to the hold-up in the circulating lines as is illustrated in Figure 7. In Figure 7 the liquid phase circulates while the vapour phase is not. When the three-way valve is switched to the position where condensed vapour phase is circulating, the composition that is circulating changes towards the more volatile component and, in isobaric runs, the temperature is lowered. By switching the valve back to the liquid sampling position the composition changes back towards the less volatile component and the initial temperature is restored. This demonstrates that even though the vapour and liquid phase compositions are equilibrium values, they are separate individual vapour and liquid points – not the vapour liquid points corresponding to each other.

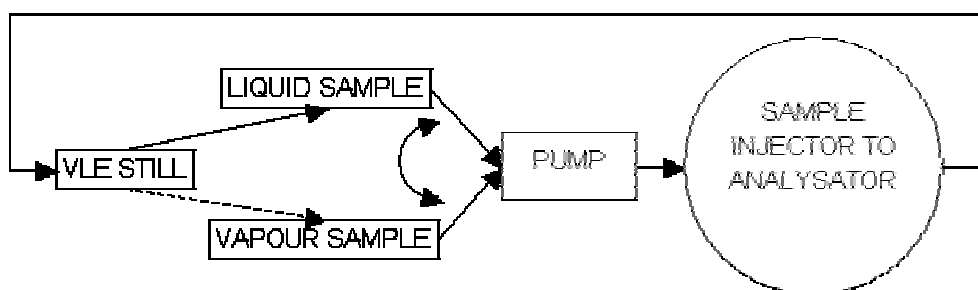


Figure 7. Schematic diagram of the sampling system in the position the liquid sample is circulated.

Mass spectrometry (MS) was tested for use in the analysis of the samples. The MS analysis system worked and the results were as good as the results obtained using gas chromatography (GC). The drawback in MS is the need for a slightly larger number of calibration mixtures than in GC. In some systems, MS analysis is superior to gas chromatography, especially for systems where the mole fraction of one component is small [49]. MS analysis could give more insight into the behaviour of molecules in the infinite dilution range due to better sensitivity than that of gas-chromatographic analysis.

The measurements of the ethanol + 2,4,4-trimethyl-1-pentene system (MS analysis) and 2-propanol + 2,4,4-trimethyl-1-pentene system (GC analysis) passed the infinite dilution test, while other systems tried did not pass this test. The measurements were found to satisfy the point test criterion except for the ethanol + 2,4,4-trimethyl-1-pentene data set. Mass spectrometry was found to be suitable for analysis both off-line and on-line, when applied to these systems.

1.14 Static total pressure apparatus

A static total pressure apparatus was built for measurements above atmospheric pressure [VI]. The target was to build a manual version of the apparatus first and gather operating experience in order to allow computer control of the apparatus later. For testing the apparatus the system 2-methylpentane + 2-butanol was selected. The measurements correspond to the results presented in [V] very well. The activity coefficients and the azeotropic composition, pressure and temperature settle within the experimental accuracy. The azeotropic compositions and temperatures for n-hexane + 2-butanol systems show definitive agreement with the results found in the literature.

Measurements were made for the 1-butene + alcohols [VIII] and cis-2-butene + alcohols [IV] systems with the same apparatus. No experimental results were found for the 1-butene + alcohol systems in the present literature. Pure component vapour pressures values agreed with those calculated from published correlations. The regression of the measurements and defining the behaviour of the dilute alcohol region pose a challenge. A small change in the activity coefficient value calculated with the model used in the regression can disguise azeotropic behaviour.

The presence of an azeotrope for the 1-butene + methanol system was found [VIII]. For the 1-butene+ethanol systems an azeotrope is probable, due to a rise in pressure in first experimental mixture point of ethanol in 1-butene compared to 1-butene vapour pressure. The pressure rise of the point is within the experimental uncertainty of the measurements, but the accuracy of the regression is worse than the experimental error in the dilute alcohol region. The Legendre-polynomial fit could not model the azeotropic behaviour. A very small change in the behaviour of the model with regard to too small an activity coefficient value can mask the azeotropic behaviour. Similar behaviour in the dilute alcohol region can also be detected for the 2-methylpentane + 2-butanol system compared to measurements made with the circulation still [VI]. Generally, the residuals of the experimental and calculated pressure have the largest values in the dilute alcohol range. Though the other systems studied show no indication of azeotropic behaviour, in these systems also the pressure residuals are largest in the dilute alcohol range.

Miyano et al. used the gas stripping method for determining the infinite dilution activity coefficient for 1-butene in methanol at 320.09 K [50]. The reported value of 9.1 for the infinite dilution activity coefficient of 1-butene is in agreement with the value determined from the Legendre-polynomial regression (8.9 at 326.18 K) of our measurements.

The behaviour of cis-2-butene + alcohols systems was similar to the 1-butene systems. Azeotropes were found for both the cis-2-butene + methanol and cis-2-butene + ethanol systems [IX].

The second phase in building the static total pressure apparatus was to develop a computer-controlled version of it. The mixing of the cell was improved, the cell volume was increased and insulation was added to the water bath. The computer control enables measurements to be made with little effort compared to the manual version of the apparatus. The drawback in this case was the reduction of the accuracy of the pressure measurement system, from ± 0.067 kPa to ± 0.2 kPa due to the limitations in the automation system. The temperature measurement accuracy was also reduced from ± 0.02 K to ± 0.03 K due to the resolution used in the recording of the temperature measurements. For example, the apparatus was used for 2-methylpropene + alcohol system measurements [X], with azeotropic behaviour found for the 2-methylpropene + methanol system. Miyano et al. used the gas stripping method for determining the infinite dilution activity coefficient for 2-methylpropene in methanol at 320.02 K [50]. His reported value of 8.9 for the infinite dilution activity coefficient of 2-methylpropene is in agreement with the value determined from the Legendre-polynomial regression (8.71 at 323.14 K) of our measurements. An even more stringent test of the experimental method and the regression of the measurements would be to compare the infinite dilution activity coefficients of the alcohol because the numerical value of the activity coefficient as well as the pressure residuals are larger in the dilute alcohol range. Unfortunately, this kind of measurements is not available at the moment.

The main source of error in calculating the amount of components injected into the equilibrium cell in a static total pressure measurement is the density correlation [VI], [VIII], [IX], [X], which is used for finding the density of the component in the pump. The uncertainty of the volume injected becomes the dominant error source only in the composition range where the amount of component in the cell is small ($x < 0.1$). The error estimates, which range from $0.01 \cdot p$ to $0.03 \cdot p$, given for the density correlation, apply to a wide range of temperature [51]. The typical temperature range of the injection pumps are from 285 K to 303 K. Comparing densities at 298.15 K, calculated from the density correlation, with values from the literature [52]-[57], led to the conclusion that the errors in density were less than $0.004 \cdot p$ for all of the alcohols and hexane. For the other components studied, the errors were less than $0.01 \cdot p$ [58]-[59]. This indicates that the accuracy of the injections of the components is better than that given in [VII] - [X].

The measurements made with the static total pressure apparatus are at least as good as the existing capability to represent the corresponding experimental results. The capability of the model representing the measurements with the activity coefficient models used for simulating the

multi-component systems (Wilson, NRTL and UNIQUAC) becomes the limiting factor: The measurements made with this apparatus are more accurate than the representation achieved with the activity coefficient models presently in use. Further study should be carried out to achieve an improvement in the regression of the measurements with the Legendre-polynomial model.

CONCLUSION

In this work, three types of apparatuses were built for the measurement of vapour liquid equilibrium (VLE). The quality of the measurements was verified with thermodynamic consistency tests, when applicable. After comparing the measured results with other published sources, which had used a variety of different experimental approaches the conclusion that the measurements were reliable was reached. The results were modelled with the so-called gamma-phi approach, when applied to the systems measured, allow the simulation of multi-component systems with the binary parameters optimised.

A static apparatus with the capability of analysing samples from the liquid and vapour phases was built. The sampling system was automated and controlled by means of the gas chromatograph software. The automated sampling system allowed the withdrawal and analysis of samples without disturbing the VLE. Measurements were reported for ethanenitrile + 2-methylpropane and ethanenitrile + 2-methylpropene systems. The measurements passed the integral test and the residuals for the Wilson equation fit was less than 0.01 in mole fraction, which is often considered as the criterion for thermodynamic consistency. The pressure residuals were smaller than the experimental uncertainty for the ethanenitrile + 2-methylpropene system. For the ethanenitrile + 2-methylpropane system, however the pressure residuals were larger than the experimental uncertainty. The reason for this result probably lies in the possible formation of two liquid phases during sample circulation in the composition range from $x(\text{ethanenitrile}) = 0.2$ to $x(\text{ethanenitrile}) = 0.8$. Two liquid phases can occur during sampling because the temperature must be lower than the equilibrium cell temperature in the sampling line in order not to cause the formation of a vapour and liquid phase split. The measured systems can be utilised in modelling the behaviour of ethanenitrile, which is a catalyst poison, in the processes utilising the C4 stream from the FCC unit. The VLE model can be used to find a cost-effective solution for ethanenitrile removal from these processes.

Following the success in constructing the previous apparatus a circulation still was built. The benefit of the apparatus is that the volume of the mixture needed for making experiments with it was only 80 cm³. It was used to obtain isobaric and/or isothermal VLE data for ten binary systems consisting of C1 to C4 –alcohols and 2,4,4-trimethyl-1-pentene and C4-alcohols + C6-alkanes. The measurements made were tested with thermodynamic consistency tests. The test results showed that the measurements made with this apparatus are of high quality.

An on-line system with circulation of the samples was tested using two analysis methods, i.e., mass spectrometry (MS) and gas chromatography (GC). The on-line system was applied to the

ethanol + 2,4,4-trimethyl-1-pentene and 2-propanol + 2,4,4-trimethyl-1-pentene system at atmospheric pressure. The measurements of the ethanol + 2,4,4-trimethyl-1-pentene system (MS analysis) and 2-propanol + 2,4,4-trimethyl-1-pentene system (GC analysis) passed the infinite dilution test, although the other systems measured did not. The measurements were found to satisfy the point test criterion except for the ethanol + 2,4,4-trimethyl-1-pentene (MS analysis) data set. When applied to those systems MS was found to be suitable for analysis both off-line and on-line.

The measurements published for the 2,4,4-trimethyl-1-pentene systems were novel and could not be found in any previous literature. The measured data offers the possibility to create a thermodynamic model for the design of processes, which contain 2,4,4-trimethyl-1-pentene.

Vapour pressure was determined with the circulation still for 2-methoxy-2,4,4-trimethylpentane. Vapour pressure measurements and VLE measurements were not available in the earlier publications for 2-methoxy-2,4,4-trimethylpentane. The enthalpy of vaporization calculated from the vapour pressure measurements of 2-methoxy-2,4,4-trimethylpentane are well in line with the value published later by other authors, showing, that it is possible to measure vapour pressure with this apparatus accurately.

While isobaric data at 101 kPa were found in existing literature for the 2-methyl-2-propanol + 2-methylpentane and 2-methyl-2-propanol + 3-methylpentane systems, the data were isothermal in the present study. No corroborating material on the 2-butanol + 2-methylpentane and the 2-butanol + 3-methylpentane systems could be discovered in the literature.

The systems measured with the circulation still are crucial in the development of processes for dimerisation of 2-methylpropene. The measurements made for 2-methoxy-2,4,4-trimethylpentane vapour pressure determination and methanol + 2-methoxy-2,4,4-trimethylpentane and methanol + 2,4,4-trimethyl-1-pentene systems VLE offer the possibility to search for an economically feasible process for the further etherification of isooctene.

A static total pressure apparatus was also built. This apparatus enables rapid determination of VLE for systems at pressures lower than 689 kPa and in the temperature range from 293 K to 368 K. Consistency testing of the results measured with this apparatus is not possible due to the experimental method used. Two binary systems were measured to test the apparatus:

2-butanol + 2-methylpentane

2-butanol + n-hexane

The 2-butanol + 2-methylpentane system measurements were compared with measurements made earlier with the circulation still and good agreement was found. The azeotropic compositions, which were determined at two temperatures for the 2-butanol + n-hexane system, agreed with the data published in other literature.

Using the manual version of the static total pressure apparatus ten binary systems consisting of C1 to C4 alcohols with C4-alkenes were measured. With the exception of one system, VLE measurements were not found in the known literature for these binary systems. The static total pressure apparatus was upgraded to a computer-controlled apparatus and measurements were made for five binary systems consisting of C1 to C4 alcohols with 2-methylpropene. VLE measurements were found for only two systems measured, but at different temperature. VLE measurements have not been published before for the other 2-methylpropene systems presented in this work. Infinite dilution activity coefficients for one system were located in the literature and they were well in line with the results obtained from the computer controlled apparatus.

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