



**Phase equilibrium studies and the blending/separation potential
of alcohol, ketone and alkane mixtures for process design
applications.**

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ABSTRACT

Ketones, alcohols and alkanes are used in various applications in the petrochemical and solvent industries and as feedstock in product development. Mixtures of these components are found in a variety of process waste and product streams. Alcohols and ketones can be used as oxygenated additives in unleaded gasoline to improve the octane number. An important consideration for the use of oxygenated compounds in the fuel industry is the separation and blending potential of these fuels with alkanes and alkenes (the main components of petrol and diesel), as this can affect their capacity to absorb water from the atmosphere, or when live steam is used in refining.

Since vapour-liquid (VLE) and liquid-liquid (LLE) phase equilibrium data are necessary to characterize the blending and separation limits or potential of normal hydrocarbon + oxygenated hydrocarbon mixtures for process design applications, such data were measured in this study. Namely, phase equilibrium data were measured for a range of binary, ternary and quaternary systems comprising these component types. The list of systems measured and conditions are: binary data for n-hexane (1) + pentan-2-one/ 4-methylpentan-2-one (2) (VLE at approximately $T = 313, 323, 334$ K); ternary data for methanol (1) + n-hexane (2) + pentan-2-one/ 4-methylpentan-2-one (3) (LLE at three isotherms each in the range of $T = 300$ to 309 K and $P = 0.1$ MPa) and quaternary data for the methanol (1) + n-hexane (2) + pentan-2-one (3) + 4-methylpentan-2-one (4) (LLE at $T = 303, 308, 313$ K and $P = 0.1$ MPa) system. n-Hexane was used as a representative component for light petrol/gasoline distillates. The behaviour of the systems is complex as they can exhibit azeotropy and partial miscibility at common process conditions.

The VLE measurements were undertaken at sub-atmospheric pressures using a dynamic apparatus under pressure control with both phases manually sampled. To confirm the procedure and equipment precision a binary isothermal VLE test measurement for the system of propan-1-ol (1) + n-heptane (2) at approximately 333 K was conducted and compared to literature with good agreement within 1 kPa, and with compositions within the standard combined experimental uncertainty of 0.005 mole fraction.

The γ - Φ regression approach was used with the non-random two-liquid (NRTL) or UNIQUAC activity coefficient models employed to account for the nonideality of the liquid phase, with the Hayden and O'Connell correlation in the virial equation of state, used to account for the vapour phase nonideality. A good correlation between the calculated and experimental pressure data was observed as the RMSD values do not exceed 0.048 kPa, which was within the experimental standard combined uncertainty in pressure of 0.1 kPa. The standard combined uncertainty in temperature was 0.1 K. The data was also modelled by the ϕ - ϕ approach with the Peng-Robinson and Perturbed-Chain Statistical Associating Fluid Theory equations of state, which resulted in an inferior performance in comparison to the modelling by the γ - Φ approach. The data was regressed by nonlinear least-squares via the Aspen Plus V10 software package. The area, point and infinite dilution tests were employed to test the thermodynamic consistency of the experimental VLE data measured in this work and the data was confirmed to be thermodynamically consistent using the conventional tolerances. Excess enthalpy predictions were found to correlate well with the cases where literature data was available and was well within 5%.

LLE experiments were undertaken by the direct analytic method using a modified doubled-walled glass cell and withdrawal of both phase samples for analysis. The experimental procedure and apparatus precision were confirmed by binary LLE test measurements for the methanol (1) + n-hexane (2) system. The standard combined uncertainty in temperature and composition was 0.1 K and 0.005 mole fraction respectively. The experimental tie lines for the LLE data were correlated using the NRTL and UNIQUAC activity coefficient models. For this modelling, the minimization of the objective function was conducted using nonlinear least-squares via the Aspen Plus software. All ternary systems studied were found to exhibit type I ternary LLE behaviour. Aspen Plus software was used to identify preliminary separation and blending limits using the resultant modelled data.

The blending and separation limits were identified by phase boundaries, and critical points such as azeotropes and plait points. Residue curve maps for the methanol + n-hexane + pentan-2-one and methanol + n-hexane + 4-methylpentan-2-one systems were generated using parameters regressed from the VLE data. These were used to identify distillation boundaries and to characterize distillation nodes. For a liquid-liquid extraction process for the separation of methanol

+ pentan-2-one/4-methylpentan-2-one mixtures, where n-hexane is being considered as an extraction solvent, the relative selectivity of using n-hexane as a solvent to remove pentan-2-one/4-methylpentan-2-one from methanol was determined. For both the ternary and quaternary mixtures, the relative selectivity (β) of n-hexane was greater than unity, with the minimum and maximum value being 1.23 and 6.41 respectively for the ternary mixtures and between 1.06 and 2.91 for the quaternary mixture. This indicates that the extraction of the ketones from methanol is feasible using n-hexane, and n-hexane was found to be more selective to pentan-2-one than 4-methylpentan-2-one. The selectivity values calculated for the quaternary system were generally lower than those obtained for the ternary systems.

DECLARATION ONE: Statement of Original Work

The work presented in this dissertation was carried out in the Thermodynamic Research Unit in the School of Engineering at the University of KwaZulu-Natal, Durban, from January 2019 to December 2020 under the supervision of Doctor K. Moodley and Professor P. Naidoo.

This dissertation is submitted as the full requirement for the degree M.Sc. (Eng.) in Chemical Engineering.

I, Thavashni Chetty, therefore declare that:

- (i) The research reported in this dissertation, except where otherwise indicated, is my original work.
- (ii) This dissertation has not been submitted for any degree or examination at any other university.
- (iii) This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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- (vi) As this thesis is submitted in the journal manuscript format, under Rule DR9 c) and d) of the University of KwaZulu-Natal, only manuscript versions of published or unpublished work are presented.

Thavashni Chetty

As the candidate's supervisor, I, Dr. K Moodley, approved this dissertation for submission.

Dr K. Moodley

As the candidate's co-supervisor, I, Prof. P. Naidoo, approved this dissertation for submission.

Prof P. Naidoo

DECLARATION TWO: Contribution to publications

Details of contribution to publications and manuscripts

1. Chetty, T., Naidoo, P. and Moodley, K., 2020. Isothermal Vapor–Liquid Equilibrium (P–x–y) Measurements and Modeling of n-Hexane+ Pentan-2-one/4-Methylpentan-2-one. Journal of Chemical & Engineering Data, 65(11), pp.5567-5580.

Contribution: I conceptualized the study, developed the experimental methodology, validated the procedure, measured modelled and analysed the data, prepared the manuscript with support from Dr K Moodley and Prof P Naidoo.

2. Chetty, T., Naidoo, P. and Moodley, K., 2020. Liquid-Liquid Phase Equilibria for methanol + n-hexane + pentan-2-one/4-methylpentan-2-one at 300-309 K (in preparation)

Contribution: I conceptualized the study, developed the experimental methodology, validated the procedure, measured modelled and analysed the data, prepared the manuscript with support from Dr K Moodley and Prof P Naidoo.

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NOMENCLATURE

Symbols

a	Intermolecular attraction force parameter in the Peng-Robinson (1976) equation of state/ fitting constant for Othmer and Tobias (1942) equation
a'	Parameter in Tsonopoulos (1974) correlation
a_i	Activity of component i
a_{ij}	NRTL/UNIQUAC model fit parameter
a^{dis}	Dispersive contribution in the PC-SAFT equation of state
a^{hc}	Hard-chain contribution in the PC-SAFT equation of state
a^{polar}	Polar contribution in the PC-SAFT equation of state
a_m	Intermolecular attraction force mixture parameter in the Peng-Robinson (1976) equation of state
A	Helmholtz free energy
A_{ij}	Parameter in Hayden and O'Connell (1975) correlation
b	Molecular size parameter in the Peng-Robinson (1976) equation of state/fitting constant for Othmer and Tobias (1942) equation
b'	Parameter in Tsonopoulos (1974) correlation
b_{ij}	NRTL/UNIQUAC model fit parameter (K)
b_m	Molecular size mixture parameter in the Peng-Robinson (1976) equation of state
b_0	Parameter in Hayden and O'Connell (1975) correlation
B	Second virial coefficient ($\text{m}^3 \cdot \text{mol}^{-1}$)/parameter in Hayden-O'Connell (1975) correlation
B^0	Parameter in the correlation of Pitzer and Curl (1957)

B^1	Parameter in the correlation of Pitzer and Curl (1957)
c	Fitting constant for Hand equation
c_1	Correlation parameter in Hayden and O'Connell (1975) correlation
c_2	Correlation parameter in Hayden and O'Connell (1975)
d	Fitting constant for Hand equation
D	Summation term in the mixing rule of Wong and Sandler (1992)
E_{ij}	Mixture parameter in Hayden and O'Connell (1975) correlation
f	Fugacity of component (kPa)
$\hat{f}_i$	Fugacity of species i in solution (kPa)
$f^{(0)}$	Term in the correlation of Tsonopoulos (1974)
$f^{(1)}$	Term in the correlation of (Tsonopoulos, 1974)
$f^{(2)}$	Term in the correlation of Tsonopoulos (1974)
G	Molar Gibbs free energy (J.mol ⁻¹)
G_{ij}	NRTL model parameter
H	Molar enthalpy (J.mol ⁻¹)
Δh_{ij}	Interaction parameter in Hayden and O'Connell (1975) correlation
K	Equilibrium constant
k_{ij}	Binary interaction parameter
l_j	Parameter in UNIQUAC model
m	Denotes the number of segments per chain in the PC-SAFT equation of state
n	Number of moles of component (moles)
P	Pressure (kPa)
P_D	Deviation pressure defined by Maher and Smith (1979) (kPa)
P_i^{sat}	Saturation pressure of component i (kPa)
p_i	Partial pressure of component i (kPa)
q	pure component area parameter in UNIQUAC model
Q	Quadratic sum of second virial coefficients

r	pure component volume parameter in UNIQUAC model
R	Universal gas constant (8.314 J. mol ⁻¹ . K ⁻¹)
R_D	Radius of gyration (Angstroms)
S	Molar entropy (J.mol ⁻¹ . K ⁻¹)
T	Temperature (K)
T_{ij}^*	Mixture parameter in Hayden and O'Connell (1975) correlation
$u_{ij} - u_{ii}$	UNIQUAC model fit parameter (J.mol ⁻¹)
V_i	Molar Volume of component i (m ³ .mol ⁻¹)
V_i^l	Saturated liquid molar volume of component i (m ³ .mol ⁻¹)
x	Liquid phase mole fraction
y	Vapour phase mole fraction
z	Overall composition/coordination number in UNIQUAC model
Z	Compressibility factor

Greek letters

α	Alpha phase/ parameter for the Peng-Robinson (1976) equation of state
α_{12}	Non-randomness parameter for the NRTL model/ Relative volatility
β	Beta phase/ Relative selectivity
γ_i	Activity coefficient of species i
δ	Residual
δ_{ij}	Cross coefficient for virial equation of state (m ³ .mol ⁻¹)
Δ	Change in
ε	Tolerance/ Denotes the depth of pair potential in the PC-SAFT equation of state (J)
$\frac{\varepsilon_{ij}}{\kappa}$	Characteristic energy for the i - j interaction (K)
ξ	Parameter in Hayden and O'Connell (1975) correlation
η_{ij}	Association parameter

κ	Characteristic constant in the Peng-Robinson (1976) equation of state
κ_0	Pure component parameter for the Peng-Robinson-Stryjek-Vera (1986) equation of state
κ_1	Pure component parameter for the Peng-Robinson-Stryjek-Vera (1986) equation of state
μ	Chemical potential (J.mol ⁻¹)/ Dipole moment (C.m)
μ_{ij}^*	Mixture interaction parameter in Hayden and O'Connell (1975) correlation
θ_j	Area fraction in the UNIQUAC mode
π	Pi phase
ρ	Density (kg.m ⁻³)
σ_{ij}	Molecular size (Angstroms)
τ_{ij}	NRTL model parameter
ϕ_i	Fugacity coefficient of species i
$\hat{\phi}_i$	Fugacity coefficient of species i in solution
ϕ^*	True species fugacity coefficient.
Φ_i	Vapour correction factor
ω	Acentric factor
∞	Property at infinite dilution

Subscripts

1	Denotes component 1
2	Denotes component 2
c	Critical property
i	Component i
j	Component j
i,j	Mixture parameter
r	Reduced property
T	Total property

Superscripts

<i>0</i>	Standard state superscript
<i>calc</i>	Calculated property
<i>D</i>	Dimerised molecules
<i>exp</i>	Experimentally determined property
<i>E</i>	Excess property
<i>F</i>	Free molecules
<i>lit</i>	A property obtained from the literature
<i>l</i>	Liquid phase
<i>R</i>	Residual property
<i>sat</i>	Property at saturation
<i>v</i>	Vapour phase

Abbreviations

<i>AAD</i>	Absolute Average Deviation
<i>EOS</i>	Equation of state
<i>FTP</i>	Fischer Tropsch Process
<i>LCST</i>	Lower critical solution temperature
<i>LLE</i>	Liquid-liquid equilibrium
<i>NRTL</i>	Non-random-two-liquid
<i>ON</i>	Octane number
<i>PC-SAFT</i>	The perturbed-chain statistical associating fluid theory
<i>PR</i>	Peng-Robinson
<i>RFG</i>	Reformulated gasoline
<i>RMSD</i>	Root Mean Square Deviation
<i>TCD</i>	Thermal conductivity detector
<i>UCST</i>	Upper critical solution temperature
<i>UNIQUAC</i>	Universal quasi-chemical activity coefficient model
<i>VLE</i>	Vapour-liquid equilibrium

Accents

$\bar{M}$	Partial property
$\hat{M}$	Mixture property

CHAPTER ONE

Introduction

The main compound classes in syncrude produced from the Fischer Tropsch Process (FTP) are conventional hydrocarbons (paraffins, olefins, aromatics) and oxygenates (alcohols, aldehydes, carboxylic acids, esters and ketones) (De Klerk, 2008). Ketones, alcohols and alkanes are found in both the product and waste streams of the process. Pentan-2-one and 4-methylpentan-2-one form part of these streams and are used in a number of industrial applications. Complex organic compounds are produced using ketones such as these as the starting chemical. They are also often used as solvents, especially in the explosives, lacquers, paints, and textiles industries, in tanning, as preservatives, and in hydraulic fluids (Alvarez et al., 2007; Lv et al., 2016; Vázquez-Ojeda et al., 2013). Alkanols, especially methanol, are used as feedstock in many chemical reaction processes. In particular, methanol is a low cost raw reactive compound, that can be derived via synthesis and which is used in the production of 2-methoxy-2-methylpropane (MTBE) (an additive to gasoline), in the production of methyl esters from vegetable oils (in blends with diesel fuel) (Mourah et al., 2010) and as a feedstock for the production of olefins (Tian et al., 2015). For these processes, the isolation of methanol, ketones and alkanes from mixed streams becomes necessary.

Separation of these mixtures can be very challenging because of the proximity of the constituent component boiling points as well as the potential to form azeotropes, while liquid-liquid phase splitting behaviour can occur in methanol-hydrocarbon mixtures at ambient temperatures, which is exaggerated in the presence of water. Therefore, the phase behaviour of these mixtures (such as FTP exit streams) must be characterized for any rigorous separation process design to assess the blending or separation limits or potential. Since some methanol-alkane mixtures exhibit partial miscibility, and ketone-alkane mixtures form azeotropes at common process conditions, the separation process alternatives for these mixtures are generally complex. These process alternatives include liquid-liquid extraction, extractive/azeotropic, heterogeneous azeotropic, pressure swing, and cryogenic distillation, (Barraza et al., 1979; Lecat, 1946; Maripuri and Ratcliff, 2007; Scheller and Rao, 1973; Takeo et al., 1979), which are key separation units that are

commonly used in industry. Process design for these operations rely heavily on experimental data as predictive methods, such as those based on group contribution are not reliable and accurate in the prediction of liquid-liquid phase behaviour in ternary systems (Marino et al., 2000). Additionally, for many systems, model binary interaction parameters for both vapour-liquid and liquid-liquid phase behaviour are not readily available in the literature without proprietary knowledge.

Methanol is one of the most common and widely used industrial solvents; thus, isolation of methanol from its mixtures is of great practical importance (Dalena et al., 2018). Since many solvents have comparable boiling points to that of methanol, and because methanol forms azeotropes with many common solvents like n-hexane, propan-2-one, benzene, n-heptane, etc. extractive/azeotropic distillation has become one of the most widely used techniques to separate methanol mixtures (Lecat, 1928). The liquid-liquid equilibrium (LLE) phase-characterization of the methanol + n-hexane + ketone systems also find application in the design of liquid-liquid extraction processes and solvent recovery. To design and assess the feasibility of these processes, vapour-liquid equilibrium data and liquid- liquid equilibrium data for these systems is required along with residue curve maps.

The alcohol, ketone and alkane mixtures present in industrial-scale fuel/chemical production processes can also be used as oxygenated additives in unleaded gasoline blends to improve the octane number (Agarwal, 2007). The proportions of the different hydrocarbons used in a blend are governed by the desired thermophysical properties of the resultant mixture. Phase equilibrium data is necessary to characterize the limits of these blending procedures. Hence, an important consideration for the use of oxygenated compounds (which generally have an affinity for water) in the fuel industry is the separation and blending potential of these fuels with alkanes and alkenes (the main components of petrol and diesel) (Araki et al., 2011; Bonner and Choi, 1974; Groysman, 2014).

The majority of typical gasoline consists of a homogeneous mixture of small, fairly lightweight hydrocarbons composed of 4 to 12 carbon atoms per molecule (commonly referred to as C₄–C₁₂) (Dabelstein et al., 2007). Therefore, n-hexane or n-heptane are often chosen as a pseudo-

component to represent the physical behaviour of gasoline (Milligan, 1924) in experimental studies. Increasing attention has been given to the further improvement of low octane number (ON) gasoline after the recent regulations imposed on leaded fuel, which was traditionally used as an anti-knock agent. High octane quality of unleaded gasoline can be obtained more easily by the addition of oxygen containing fuel components (Dabelstein et al., 2007). The advantage of adding oxygenates, such as methanol, and ketones to gasoline is that they contribute very little to air pollution when they burn and are generally regarded as cleaner fuels (Demirbas et al., 2015). The US Department of Energy has identified C₄ and C₅ ketones (butan-2-one and pentan-2-one) as potential blending agents for fuels applied to Advanced Spark Ignition Engines (Miles, 2016).

The aim of this work was to investigate the separation and blending potential of alkane + alcohol + ketone mixtures found in process streams. Key objectives of the study include: (i) perform a literature review to assess the system combinations and conditions; (ii) perform phase equilibrium measurements for the relevant binary, ternary and quaternary mixtures (iii) apply thermodynamic modelling of the measured data and evaluate its consistency (iv) identify preliminary separation and blending limits from the data for process design.

In this study, to address the shortages of phase equilibrium data required for the various processes described above, phase equilibrium data of n-hexane with various oxygenates were measured, where n-hexane was used as a representative component for petrol (gasoline). A replica of a modified low pressure vapour-liquid equilibrium still of Raal and Mühlbauer (1998) originally commissioned by (Joseph et al., 2001) was used to measure isothermal vapour-liquid equilibrium data of n-hexane with C₅ and C₆ ketones. Additionally, isothermal liquid-liquid equilibrium measurements were performed for the methanol-n-hexane and methanol-n-hexane-ketone systems using the modified apparatus of (Raal and Brouckaert, 1992) commissioned initially by (Ndlovu, 2005).

Phase equilibrium data were measured for a range of binary, ternary and quaternary systems comprising the key components. The list of systems measured, and conditions are:

- i. binary isothermal VLE data for n-hexane (1) + pentan-2-one (2) system (at $T = 313.3, 323.3,$ and 333.5 K)
- ii. binary isothermal VLE data for hexane (1) + 4-methylpentan-2-one (2) system (at $T = 313.3, 323.3,$ and 333.6 K)
- iii. ternary isothermal LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system (at $T = 300.3, 303.2$ and 307.3 K and $P = 0.1$ MPa)
- iv. ternary isothermal LLE data for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system (at $T = 303.4, 308.1$ and 309.0 K and $P = 0.1$ MPa)
- v. quaternary isothermal LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) + 4-methylpentan-2-one (4) system (at $T = 303.2, 308.2$ and 313.2 K and $P = 0.1$ MPa)

These temperatures were selected for practical and economic purposes such as maintaining process design limits within atmospheric pressure and widely used process temperatures, which is common for distillation and liquid-liquid extraction operations.

The overview of the thesis is as follows: in Chapter Two of this work, the theory regarding the thermodynamic principles of phase equilibria and modelling is presented. In Chapter Three, a brief review of the techniques and equipment used for low pressure vapour-liquid and liquid-liquid equilibrium measurements is given and the equipment and procedure used in this work is discussed. Chapter Four is comprised of a published manuscript “Isothermal Vapor–Liquid Equilibrium (P – x – y) Measurements and Modeling of n-Hexane + Pentan-2-one/4-Methylpentan-2-one”. In this manuscript, VLE data measurements and data regression were performed for the binary mixtures of n-hexane (1) + pentan-2-one (2)/4-methylpentan-2-one (2) as part of this study. Chapter Five of this work is comprised of a prepared manuscript titled ‘Liquid-Liquid Phase Equilibria for methanol + n-hexane + pentan-2-one/4-methylpentan-2-one at 300-309 K’. In this manuscript, ternary LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3)/ 4-methylpentan-2-one (3) systems are presented. Ternary LLE data for these systems have not been published in the literature to date, and the publication of this manuscript is in progress. Chapter 6 provides the culminating discussion in which results from the study, separation and blending limits thereof is discussed.

Note that because the manuscript thesis format is used, there is a degree of repetition among sections that was unavoidable to allow for selected chapters to stand alone.

CHAPTER TWO

Background and review of thermodynamic principles

The design and optimization of separation processes such as distillation, extraction, leaching, adsorption and absorption require phase equilibrium data (Avoseh, 2015). Multi-component phase equilibrium data are preferred for the design of separation processes however phase equilibrium measurements are generally carried out for binary systems as measurements for multi-component systems are difficult and frequently impractical. Therefore, multi-component properties are generally computed from binary data using local composition theory. This method generally works well for vapour-liquid equilibria (VLE) but can be unreliable for the prediction of liquid-liquid equilibria (LLE) in multicomponent systems. This is because some binary pairs in the multicomponent mixture may not exhibit LLE behaviour, and so binary parameters derived from VLE data would have to be used in the multicomponent prediction. Because the order of magnitude of the excess Gibbs energy for systems exhibiting LLE is usually much greater than that for systems in VLE, activity coefficient models with a single set of binary interaction parameters per pair are unable to simultaneously capture multicomponent VLE and LLE behaviour (Rarey, 2005). Reliable ternary liquid-liquid equilibrium (LLE) data are therefore also necessary to characterize multi-component phase equilibrium properties for the design and evaluation of industrial units for extraction processes (Vakili-Nezhaad et al., 2004). The theoretical treatment of vapour-liquid and liquid-liquid phase equilibrium data allows for the prediction of the dependence of temperature and pressure on the multicomponent phase behaviour to facilitate the reliable extrapolation and interpolation of separation and blending limits at desired conditions.

This chapter provides a review of the theoretical principles of sub-atmospheric VLE and atmospheric pressure LLE data correlation and analyses. For a more detailed review of the treatment of phase equilibrium data, the reader is referred to chemical thermodynamic texts such as (Walas, 2013), (Prausnitz et al., 1999) and (Smith et al., 2001). A brief insight into blending processes in petrochemical refineries are also highlighted at the end of this chapter.

2.1. The criterion for phase equilibrium

According to Smith et al. (2001), phase equilibrium is described as a state in which there is no macroscopic change in a closed system of phases. At equilibrium, properties such as pressure (P), temperature (T) and composition of component i (x_i) undergo only differential changes. The properties of the system in equilibrium can be used to describe the properties of each phase that is in equilibrium by the use of thermodynamic relations.

A fundamental criterion for phase equilibria is the equality of chemical potential (μ_i) in each phase. For a closed system with two phases α and β , the condition for equilibrium is:

$$\mu_i^{(\alpha)} = \mu_i^{(\beta)} \quad \dots\dots\dots (i=1, 2, \dots N) \quad (2.1)$$

However, there are no absolute measurable values for chemical potential so therefore the fugacity (f), which has the units of pressure, can be related to chemical potential at constant pressure. This can be done through fugacity in solution ($\hat{f}_i$) and activity (a_i), (when only liquid phases in equilibrium are considered).

The fugacity in solution, ($\hat{f}_i$) is defined by the following expression and represents the departure in chemical potential from a standard state (denoted with superscript (0)):

$$\mu_i - \mu_i^0 = RT \ln \left[\frac{\hat{f}_i}{f_i^0} \right] \quad (2.2)$$

Activity (a_i) can be defined as the ratio of the fugacity of a substance in solution to its fugacity in some defined standard state. The activity (a_i) of a species in solution can be expressed as:

$$a_i = \frac{\hat{f}_i}{f_i^0} \quad (2.3)$$

The activities of two phases are equal if the standard fugacity (f_i^0) is the same. Therefore, for two phases α and β in which the fugacities in the standard states are equal at phase equilibrium:

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \quad (2.4)$$

2.2. Fugacity and the fugacity coefficient

Fugacity is a parameter related to the chemical potential and measurable properties. Chemical potential is the partial molar property of Gibbs energy. These thermodynamic quantities cannot be measured. From equation 2.4, for component i in vapour-liquid equilibrium, the vapour phase fugacity equals the liquid phase fugacity:

$$\hat{f}_i^v = \hat{f}_i^l \quad (i = 1, 2, \dots, N) \quad (2.5)$$

The fugacity of a component in a mixture can be described as a function of measurable quantities such as temperature, pressure, and phase composition.

For the vapour phase, the fugacity of component i in solution ($\hat{f}_i^v$) is given by:

$$\hat{f}_i^v = y_i \hat{\phi}_i P \quad (2.6)$$

Where P is the total pressure, y_i is the mole fraction and $\hat{\phi}_i$ is the fugacity coefficient in solution. The fugacity coefficient of species i in solution ($\hat{\phi}_i$) is a dimensionless function and is used to account for the non-ideality of the vapour phase.

The liquid phase fugacity is related to measurable quantities by defining a dimensionless quantity γ_i , the activity coefficient, which accounts for the liquid phase non-ideality:

$$\hat{f}_i^l = x_i \gamma_i f_i \quad (2.7)$$

Where f_i is fugacity of a pure compound.

A comparison to equation 2.3 defines a_i as:

$$a_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) = x_i \gamma_i \quad (2.8)$$

Activities and activity coefficients are discussed further in section 2.6.

For the liquid phase, the pure component fugacity f_i , is given by equation 2.9 when the liquid is assumed to be incompressible:

$$f_i = \phi_i^{sat} P_i^{sat} \exp \left[\frac{V_i^l (P - P_i^{sat})}{RT} \right] \quad (2.9)$$

The exponential term is known as the Poynting factor. This allows for the correction of liquid phase fugacity from the reference pressure (saturated vapour pressure) to the system pressure (Smith et al., 2001).

The fugacity coefficient of either a saturated liquid or saturated vapour in equilibrium is given by:

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}} \quad (2.10)$$

For vapour-liquid equilibrium of a pure component:

$$\phi_i^v = \phi_i^l = \phi_i^{sat} \quad (2.11)$$

2.3. Fugacity coefficients from the virial equation of state

Fugacity coefficients of a component in the vapour phase can be calculated from different types of equations of state such as the virial equation of state or cubic equations of state. The virial equation of state is applicable to low to moderate pressure systems (Walas, 2013).

The virial equation of state truncated after the second term is:

$$Z = 1 + \frac{BP}{RT} \quad (2.12)$$

Z is a dimensionless quantity known as the compressibility factor. For an ideal gas, $Z = 1$. B is the second virial coefficient and is a function of temperature and composition.

For mixtures, the relationship between the second virial coefficient ($B_{mixture}$) and the vapour composition is:

$$B_{mixture} = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij}(T) \quad (2.13)$$

Where i, j are the component species, y is the mole fractions of species in the gas mixture, B_{ij} is the cross-virial coefficient and is the bimolecular interaction between molecules i and j , hence $B_{ij} = B_{ji}$.

When the virial equation of state truncated to the second term is used to describe the vapour phase non-ideality, the fugacity coefficient for component i in solution is:

$$\hat{\phi}_i = \exp \left[\frac{(B_{ii} - V_i^l)(P - P_i^{sat}) + P y_j^2 \delta_{ij}}{RT} \right] \quad (2.14)$$

Where:

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2.15)$$

2.4. Correlations for the 2nd virial coefficient

Several methods have been developed for the calculation of the second virial coefficient values such as the correlations of Pitzer and Curl (1957), (Nothnagel et al., 1973), Tsonopoulos (1974) and Hayden and O'Connell (1975). The method of Hayden and O'Connell (1975) is relatively simple and applicable to various compounds of associating systems. The Hayden and O'Connell correlation builds on the work of Pitzer and Curl (1957) and Tsonopoulos (1974) and has been selected for this project as the vapour phase of alcohol ketone systems are known to be self and cross associating.

2.4.1. Pitzer and Curl, Nothnagel and Tsonopoulos

Pitzer and Curl (1957) proposed the following relation:

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \quad (2.16)$$

Where ω is the acentric factor and the second virial coefficient, B , is a function of reduced temperature T_r ,

$$T_r = \frac{T}{T_c} \quad (2.17)$$

The parameters B^0 and B^1 are given by:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (2.18)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{1.6}} \quad (2.19)$$

The acentric factor ω is a measure of the non-sphericity of a molecule. According to Reid et al. (1988) it is defined as:

$$\omega = -\log P_r^{sat} (at T_r = 0.7) - 1.000 \quad (2.20)$$

where P_r^{sat} is the reduced vapour pressure given by:

$$P_r^{sat} = \frac{p^{sat}}{P_c} \quad (2.21)$$

Applied to mixtures, Prausnitz et al. (1999) later proposed a generalized equation which includes the cross coefficients:

$$B_{ij} = \frac{RT_{cij}}{P_{cij}} (B^0 + \omega_{ij} B^1) \quad (2.22)$$

The cross-coefficient parameters are calculated from the following empirical mixing rules proposed by Prausnitz et al. (1999):

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad (2.23)$$

$$T_{cij} = \sqrt{(T_{ci} T_{cj})} (1 - \kappa_{ij}) \quad (2.24)$$

$$P_{cij} = \frac{Z_{cij}RT_{cij}}{V_{cij}} \quad (2.25)$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \quad (2.26)$$

$$V_{cij} = \left(\frac{V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}}}{2} \right)^3 \quad (2.27)$$

κ_{ij} in equation 2.24 is a binary interaction parameter. It is set to zero if i and j are similar in size and chemical nature.

The Tsonopoulos (1974) correlation uses a modified form of the Pitzer-Curl correlation and can be used for calculating virial coefficients for both polar and non-polar compounds.

For non-polar gases, Tsonopoulos (1974) suggests:

$$\frac{BP_c}{RT_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (2.28)$$

Where:

$$f^{(0)}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \quad (2.29)$$

and

$$f^{(1)}(T_r) = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \quad (2.30)$$

In polar compounds, an additional parameter is included in Equation 2.28:

$$\frac{BP_c}{RT_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + f^{(2)}(T_r) \quad (2.31)$$

Where the last term incorporates the polar effects and is given by:

$$f^{(2)}(T_r) = \frac{a'}{T_r^6} \quad (2.32)$$

For hydrogen bonding compounds, dimerization in the vapour phase results in an increased complexity hence the last term in equation 2.31 is given by:

$$f^{(2)}(T_r) = \frac{a'}{T_r^6} - \frac{b'}{T_r^8} \quad (2.33)$$

The parameters a' and b' are functions that are dependent on the dipole moments and differ for different compounds. They are found by regression of experimental volumetric data for similar compounds.

The same mixing rules for T_{cij} and ω_{ij} are used as in the Pitzer and Curl (1957) correlation.

However, for P_{cij} Tsionopoulos (1974) proposed the equation:

$$P_{cij} = \frac{4T_{cij} \left(\frac{P_{ci}V_{ci}}{T_{ci}} + \frac{P_{cj}V_{cj}}{T_{cj}} \right)}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \quad (2.34)$$

For polar/non-polar systems, it is assumed that B_{ij} has no polar term and a_{ij} and b_{ij} are set equal to zero. For polar/polar systems, B_{ij} can be determined using $a_{ij} = 0.5(a_i + a_j)$ and $b_{ij} = 0.5(b_i + b_j)$.

Nothnagel (1973) introduced a correlation for determining fugacity coefficients by applying the chemical theory of vapour imperfections.

According to Prausnitz et al. (1980), the equation of chemical equilibrium is given as:

$$K_{ij} = \frac{1}{P} \frac{z_{ij}}{z_i z_j} \frac{\phi_{ij}^*}{\phi_i^* \phi_j^*} = \frac{-B_{ij}^D(2-\delta_{ij})}{RT} \quad (2.35)$$

where K_{ij} is the equilibrium constant, z is the true mole fraction of the species in equilibrium, P is the system pressure and ϕ^* is the true species fugacity coefficient.

For $i \neq j$, δ_{ij} is equal to 0 and for $i = j$ it is equal to 1.

ϕ_i can be calculated from:

$$\phi_i = \frac{z_i \phi_i^*}{y_i} \quad (2.36)$$

Where y_i is the apparent vapour phase mole fraction of species i .

The Lewis fugacity rule is assumed to be applicable, therefore:

$$\ln \phi_i^* = \frac{P B_i^F}{RT} \quad (2.37)$$

Superscript F refers to the relatively “free” molecules (weak physical forces).

2.4.2. The Hayden-O’Connell correlation

Hayden and O’Connell (1975) proposed a methodology that is widely employed for evaluation of second virial coefficients. The methodology encompasses a comprehensive range of compounds including associating, nonpolar and polar compounds. The correlation was developed based on intermolecular interactions existing between molecule pairs. The HOC formulation employs the chemical theory of dimerization and accounts for strong association and solvation effects that include those found in systems with oxygenates (Pillay, 2009). Pure component properties such as the dipole moment μ_d , critical temperature T_c , critical pressure P_c , mean radius of gyration R_d and the solvation and association parameter η , are required for the calculation of this correlation.

The correlation assumes the virial coefficient to be the sum of two types of interactions:

$$B_{ij} = B_{ij}^F + B_{ij}^D \quad (2.38)$$

Superscript F refers to the relatively “free” molecules (weak physical forces), and D refers to the “bound” or “dimerised” molecules (“chemical” forces).

$$B_{ij}^F = (B_{nonpolar}^F)_{ij} + (B_{polar}^F)_{ij} \quad (2.39)$$

$$B_{ij}^D = (B_{metastable})_{ij} + (B_{bond})_{ij} + (B_{chemical})_{ij} \quad (2.40)$$

Temperature-dependent correlations are used to calculate individual contributions to the second virial coefficient:

$$(B^F_{nonpolar})_{ij} = b_{0ij} \left(0.94 - \frac{1.47}{T_{ij}^{*'}} - \frac{0.85}{T_{ij}^{*'}^2} - \frac{1.015}{T_{ij}^{*'}^3} \right) \quad (2.41)$$

$$(B^F_{polar})_{ij} = b_{0ij} \mu_{ij}^{*'} \left(0.74 - \frac{3.0}{T_{ij}^{*'}} - \frac{2.1}{T_{ij}^{*'}^2} - \frac{2.1}{T_{ij}^{*'}^3} \right) \quad (2.42)$$

$$(B_{metastable})_{ij} + (B_{bond})_{ij} = b_{0ij} A_{ij} \exp \left(\frac{\Delta h_{ij}}{T_{ij}^*} \right) \quad (2.43)$$

$$(B_{chemical})_{ij} = b_{0ij} E_{ij} \left[1 - \exp \left(\frac{1500 \eta_{ij}}{T} \right) \right] \quad (2.44)$$

$$\frac{1}{T_{ij}^{*'}} = \frac{1}{T_{ij}^*} - 1.6 \omega_{ij} \quad (2.45)$$

$$T_{ij}^* = \frac{T}{\left(\frac{\varepsilon_{ij}}{\kappa} \right)} \quad (2.46)$$

The temperature-independent parameters used in equations 2.41 to 2.46 are:

$$b_{0ij} = 1.26184 \sigma_{ij}^3 \quad (2.47)$$

$$\begin{aligned} \mu_{ij}^{*'} &= \mu_{ij}^* && \text{if } \mu_{ij}^* < 0.04 \\ &= 0 && \text{if } 0.04 \leq \mu_{ij}^* < 0.25 \\ &= \mu_{ij}^* - 0.25 && \text{if } 0.25 \leq \mu_{ij}^* \end{aligned} \quad (2.48)$$

$$A_{ij} = -0.3 - 0.05 \mu_{ij}^* \quad (2.49)$$

$$\Delta h_{ij} = 1.99 + 0.2 \mu_{ij}^{*2} \quad (2.50)$$

$$\mu_{ij}^* = \frac{7243.8 \mu_i \mu_j}{\left(\frac{\varepsilon_{ij}}{\kappa} \right) \sigma^3} \quad (2.51)$$

$$E_{ij} = \exp \left\{ \eta_{ij} \left(\frac{650}{\left(\frac{\varepsilon_{ij}}{\kappa} \right) + 300} - 4.27 \right) \right\} \text{ for } \eta_{ij} < 4.5 \quad (2.52a)$$

Or

$$E_{ij} = \exp \left\{ \eta_{ij} \left(\frac{42800}{\left(\frac{\varepsilon_{ij}}{\kappa} \right) + 22400} - 4.27 \right) \right\} \quad \text{for } \eta_{ij} > 4.5 \quad (2.52b)$$

Where, T is the temperature (K), $\frac{\varepsilon_{ij}}{\kappa}$ is the characteristic energy for the i - j interaction (K), σ_{ij} is the molecular size (Angstroms), μ_{ij} is the dipole moment of component i (Debye), η_{ij} is the association parameter when ($i = j$) or the solvation parameter when ($i \neq j$) and ω_{ij} is the nonpolar acentric factor

For i - j , parameters $\left(\frac{\varepsilon_{ii}}{\kappa} \right)$, σ_{ii} and ω_{ii} are predicted from pure component properties:

$$\omega_{ii} = 0.006026 R_{Di} + 0.02096 R_{Di}^2 - 0.001366 R_{Di}^3 \quad (2.53)$$

$$\left(\frac{\varepsilon_{ii}}{\kappa} \right) = \left(\frac{\varepsilon_{ii}}{\kappa} \right)' \left\{ 1 - \xi c_1 \left[1 - \frac{\xi (1+c_1)}{2} \right] \right\} \quad (2.54)$$

$$\sigma_{ii} = \sigma_{ii}' (1 + \xi c_2)^{1/3} \quad (2.55)$$

$$\left(\frac{\varepsilon_{ii}}{\kappa} \right)' = T_{ci} \left[0.748 + 0.91 \omega_{ii} - \frac{0.4 \eta_{ii}}{2 + 20 \omega_{ii}} \right] \quad (2.56)$$

$$\sigma_{ii} = (2.44 - \omega_{ii}) \left(1.0133 \frac{T_{ci}}{P_{ci}} \right)^{1/3} \quad (2.57)$$

$$\xi = 0 \quad \text{for } \mu_i < 1.45 \quad (2.58a)$$

$$\xi = \frac{1.7941 \times 10^7 \mu_i^4}{\left[\left(2.882 - \frac{1.882 \omega_{ii}}{(0.03 + \omega_{ii})} \right) T_{ci} \sigma_{ii}'^6 \left(\frac{\varepsilon_{ii}}{\kappa} \right) \right]} \quad \text{for } \mu_i \geq 1.45 \quad (2.58b)$$

$$c_1 = \frac{16 + 400 \omega_{ii}}{10 + 400 \omega_{ii}} \quad (2.59)$$

$$c_2 = \frac{3}{10 + 400 \omega_{ii}} \quad (2.60)$$

Pure component properties that are required for equations 2.53 to 2.60 include T_{ci} , the critical temperature of component i (K), P_{ci} , the critical pressure of component i (bar) and R_{Di} , the mean radius of gyration of component i (Angstroms).

The cross parameters $\left(\frac{\varepsilon_{ij}}{\kappa}\right)$, σ_{ij} and ω_{ij} ($i \neq j$) are calculated using suitable mixing rules and pure component parameters given by equations 2.61 to 2.63:

$$\omega_{ij} = \frac{1}{2} (\omega_{ii} + \omega_{jj}) \quad (2.61)$$

$$\left(\frac{\varepsilon_{ij}}{\kappa}\right) = \left(\frac{\varepsilon_{ij}}{\kappa}\right)' (1 + \xi' c_1') \quad (2.62)$$

$$\sigma_{ij} = \sigma_{ij}' (1 - \xi' c_2') \quad (2.63)$$

Where

$$\left(\frac{\varepsilon_{ij}}{\kappa}\right)' = 0.7 \left[\left(\frac{\varepsilon_{ii}}{\kappa}\right) \left(\frac{\varepsilon_{jj}}{\kappa}\right) \right]^{1/2} + \frac{0.6}{\left[\frac{1}{\left(\frac{\varepsilon_{ii}}{\kappa}\right)} + \frac{1}{\left(\frac{\varepsilon_{jj}}{\kappa}\right)} \right]} \quad (2.64)$$

$$\sigma_{ij}' = (\sigma_{ii} \sigma_{jj})^{1/2} \quad (2.65)$$

$$\xi' = \frac{\mu_i^2 \left(\frac{\varepsilon_{jj}}{\kappa}\right)^{\frac{2}{3}} \sigma_{ij}^4}{\left(\frac{\varepsilon_{ii}}{\kappa}\right) \sigma_{ij}'^6} \quad \text{for } \mu_i \geq 2 \text{ and } \mu_j = 0 \quad (2.66a)$$

Or

$$\xi' = \frac{\mu_j^2 \left(\frac{\varepsilon_{kk}}{\kappa}\right)^{\frac{2}{3}} \sigma_{ij}^4}{\left(\frac{\varepsilon_{ii}}{\kappa}\right) \sigma_{ij}'^6} \quad \text{for } \mu_j \geq 2 \text{ and } \mu_i = 0 \quad (2.66b)$$

Or

$$\xi' = 0 \quad \text{for all values of } \mu_i \text{ and } \mu_j \quad (2.66c)$$

$$c_1' = \frac{16+400\omega_{ij}}{10+400\omega_{ij}} \quad (2.67)$$

$$c_2' = \frac{3}{10+400\omega_{ij}} \quad (2.68)$$

The Hayden O'Connell correlation is of course only applicable for low to moderate pressures because the truncated second virial equation does not hold for systems at high pressures.

2.5. Equations of State

Cubic equations of state are regarded as the simplest method of describing both liquid and vapour behaviour. With the use of a suitable mixing rule in conjunction with these equations of state, non-ideal chemical systems can be accurately described. Statistical Associating Fluid Theory are becoming more popular in industry, as these models are versatile and have been successfully applied to a wide range of physical property predictions for mixtures (Gross and Sadowski, 2001). In this work, the Peng–Robinson equation of state (Peng and Robinson, 1976) (PR) and the Perturbed-Chain Statistical Associating Fluid Theory (Gross and Sadowski, 2001) (PC-SAFT) equation of state was also used to model the experimental data using the ϕ - ϕ formulation.

2.5.1. The Peng-Robinson equation of state

The equation of state proposed by Peng and Robinson (1976) assumes that the constituent molecules occupy a finite volume and is a modification of the original Van der Waals (1910) equation of state and was intended to improve the accuracy of the prediction of liquid densities and critical region behaviour. It generally employs a single binary interaction parameter and is given in the pressure explicit form as:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{(V_m + b(1 - \sqrt{2}))(V_m + b(1 + \sqrt{2}))} \quad (2.69)$$

where

$$a(T) = [a(T_c)][\alpha(T_r, \omega)] \quad (2.70)$$

$$b(T) = b(T_c) \quad (2.71)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (2.72)$$

$$b(T_c) = 0.07780 \frac{RT_c}{P_c} \quad (2.73)$$

$$\alpha(T_r, \omega) = [1 + (\kappa_0 + \kappa_1(1 + \sqrt{T_r})(0.7 - T_r))(1 - \sqrt{T_r})]^2 \quad (2.74)$$

$$\kappa_0 = (0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3) \quad (2.75)$$

Since association is not very significant in the alkane + ketone systems considered for VLE measurement, employing further modifications to the PR model, such as those of Stryjek and Vera (1986) was not considered necessary.

The fugacity coefficient in solution can be calculated from:

$$\ln \hat{\phi}_i = \frac{\bar{b}_i}{b} (Z - 1) - \ln \left(\frac{Z(V_m - b)}{V_m} \right) - \frac{a(T)}{(-2\sqrt{2})bRT} \left(1 + \frac{\bar{a}_i}{a} - \frac{\bar{b}_i}{b} \right) \ln \left(\frac{(V_m + \sigma b)}{V_m + \varepsilon b} \right) \quad (2.76)$$

Where $\bar{a}_i$ and $\bar{b}_i$ are the partial properties of a and b respectively and σ and ε are model specific parameters.

2.5.2. Mixing rules for cubic equations of state

Mixing rules are important in the implementation of equations of state for the representation of vapour-liquid equilibrium data. Equations of states can be extended from a pure-component form into a multicomponent mixture form through the use of an appropriate mixing rule. The mixing rules used in the equations of state will determine the interaction of molecules in the system. There are many different types of mixing rules available for use with the van der Waals one-fluid-theory classical mixing rule being the simplest. A more detailed analysis of the types of mixing rules available in thermodynamics is available in Raal and Mühlbauer (1998). This study focuses on the application of the Wong and Sandler (1992) mixing rules.

2.5.2.1. The Wong-Sandler Mixing Rule for use in the Peng-Robinson equation of state

The mixing rule for cubic equations of state developed by Wong and Sandler (1992) is density-independent and accurately correlates VLE data and assumes the infinite pressure limit. This mixing rule can be applied to both simple and complex systems which consist of polar and associating components. An activity coefficient model such as NRTL (Renon and Prausnitz,

1968) or UNIQUAC (Abrams and Prausnitz, 1975) etc. is required to calculate the excess Helmholtz free energy (A^E). By use of A^E , quadratic composition dependence for the second virial coefficient is ensured which is consistent with statistical mechanics (Raal and Mühlbauer, 1998). The correct use of the Helmholtz free energy at infinite pressure also enables the Wong-Sandler mixing rules to be correct at low or high densities without being density dependent.

In the mixing rule of Wong-Sandler, the mixture parameters a_m and b_m are:

$$\frac{a_m}{RT} = \frac{QD}{(1-D)} \quad (2.77)$$

$$b_m = \frac{Q}{(1-D)} \quad (2.78)$$

Where Q and D are defined as:

$$Q = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (2.79)$$

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{cRT} \quad (2.80)$$

A_∞^E is the excess Helmholtz free energy calculated at infinite pressure.

According to Wong and Sandler (1992), the excess Helmholtz free energy, A^E , is much less pressure dependent than the excess Gibbs free energy, G^E , therefore the correct behaviour is obtained at very low and infinite pressures. The principle that the excess Helmholtz free energy A^E is a weak function of pressure was used, therefore its value at infinite pressure is equivalent to that of excess Gibbs free energy, G^E at low pressure. Hence, high pressure vapour-liquid equilibrium can be predicted from low pressure vapour-liquid equilibrium data. Excess Helmholtz free energy and excess Gibbs free energy are also interchangeable at constant temperature. For additional equations and derivations on this mixing rule, the reader is referred to Wong and Sandler (1992).

In this work, the NRTL excess Gibbs energy model was used to describe A^E as follows:

$$\frac{A_{\infty}^E}{RT} = \sum_i x_i \left(\frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} \right) \quad (2.81)$$

$$\ln \gamma_i^{\infty} = \frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} + \sum_j \frac{x_j g_{ij}}{\sum_k x_k g_{kj}} \left(\tau_{ij} - \frac{\sum_l x_l \tau_{lj} g_{lj}}{\sum_k x_k g_{ki}} \right) \quad (2.82)$$

The cross parameter is calculated as follows:

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right)}{2} (1 - k_{ij}) \quad (2.83)$$

The binary interaction parameter, k_{ij} is obtained from the regression of binary vapour-liquid equilibrium experimental data.

2.5.3. The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state

The perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (Gross and Sadowski, 2001) employs a modification to the SAFT theory of Huang and Radosz (1990) and employs the perturbation theory developed by Barker and Henderson (1967).

In the Helmholtz energy explicit format, the energetic components of the equation of state are comprised of three terms:

$$a^{res} = a^{hc} + a^{dis} + a^{polar} \quad (2.84)$$

Where a^{hc} , a^{dis} , a^{polar} are the hard-chain, dispersive and polar contributions, given by:

$$\frac{a^{hc}}{RT} = m \frac{a^{hs}}{RT} - \sum_i x_i (m_i - 1) \ln g_{ii}^{hs}(\sigma_{ii}) \quad (2.85)$$

$$\frac{a^{hs}}{RT} = \frac{1}{\xi_o} \left[\frac{3\xi_1\xi_2}{(1-\xi_3)} + \frac{\xi_2^3}{\xi_3(1-\xi_3^2)} + \left(\frac{\xi_2^3}{\xi_3^2} - \xi_o \right) \ln(1 - \xi_3) \right] \quad (2.86)$$

$$\frac{a^{dis}}{RT} = -2\pi\rho m^2 \left(\frac{\epsilon}{kT} \right) \sigma^3 I_1 - \pi\rho m^3 C I_2 \left(\frac{\epsilon}{kT} \right)^2 \sigma^3 \quad (2.87)$$

$$\frac{a^{polar}}{RT} = m \frac{a_2^{polar}/RT}{1 - a_3^{polar}/a_2^{polar}} \quad (2.88)$$

Where m , is the number of segments per chain, σ is the segment diameter in Armstrong, and ε is the depth of pair potential in joules. Intermediate parameters are defined in the original publication of Gross and Sadowski (2001).

For mixtures, the following mixing rules apply:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (2.89)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij}) \quad (2.90)$$

Where, k_{ij} , the parameter characterizing binary interactions for unlike chains, is included to adjust for segment-segment interactions.

2.6. Activity and activity coefficient

Activity (a_i) of a species in solution is given by equation 2.3:

$$a_i = \frac{\hat{f}_i}{f_i^o} \quad (2.3)$$

The activity coefficient concept was introduced to account for deviation from ideality of a liquid phase for phase equilibrium calculations. The ideal reference state for a liquid is the ideal solution, which is distinct from the ideal gas reference state, as molecules in the ideal gas reference state do not exert force on one another. According to Gess et al. (1991), in order to obtain some physical sense of the activity coefficient, the concept of excess properties, which describe the departure of the liquid phase from ideality, must be introduced. An excess property is defined as “the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition” (Halder, 2014).

The fundamental excess property relation as derived by Smith et al. (2001) is given by:

$$d \left(\frac{nG^E}{RT} \right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \ln \gamma_i dn_i \quad (2.91)$$

G^E is the molar excess Gibbs energy, V^E is the molar excess volume, and H^E is the molar excess enthalpy.

As a consequence of the definition of chemical potential, γ_i is given by:

$$\ln \gamma_i = \left[\frac{\partial \left[n \left(\frac{G^E}{RT} \right) \right]}{\partial n_i} \right]_{T,P,n_{j=1}} \quad (2.92)$$

The activity coefficient for a component i is related to the pure component and mixture fugacity in solution by rearranging equation 2.7:

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^o} \quad (2.93)$$

The relationship between the excess Gibbs energy and the activity coefficient can be expressed through the summability relationship as:

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i \quad (2.94)$$

2.6.1. Liquid phase activity coefficient models

Prausnitz et al. (1999) states that many equations have been proposed for the relation between activity coefficients and mole fractions. The models used in this project to model the equilibrium data of the liquid phase were the NRTL model (Renon and Prausnitz, 1968) and UNIQUAC model (Abrams and Prausnitz (1975)). These models assume that the local composition around molecule i is independent of the local composition around molecule j (local composition). Their merits are discussed below.

2.6.1.1. The Non-Random Two-Liquid (NRTL) model

The NRTL model uses the two-cell theory, where interactions of component i with component j are treated differently from those of component j with component i . The NRTL model can accurately describe highly non-ideal systems and is capable of representing partial liquid miscibility (liquid-liquid equilibrium). The NRTL equation can be extended to multicomponent systems and its parameters can have explicit temperature dependence. The NRTL equations applicable to binary systems are given in equations 2.95 to 2.101 as shown by Smith et al. (2001):

$$\frac{G^E}{RT} = \sum_{i=1}^m x_i \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} \quad (2.95)$$

The activity coefficients derived from this equation are

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{G_{ij} x_j}{\sum_{l=1}^m G_{lj} x_l} \left[\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right] \quad (2.96)$$

Where:

$$\tau_{ji} = \left(\frac{g_{ji} - g_{ii}}{RT} \right) \quad (2.97)$$

And a temperature dependent τ_{ji} is given by:

$$\tau_{ji} = \left(a_{ji} + \frac{b_{ji}}{T} \right) \quad (2.98)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (2.99)$$

Where:

$$a_{ji} = a_{ij} \quad (2.100)$$

$$G_{ii} = G_{jj} = 1 \quad (2.101)$$

τ_{ij} represents the case of interaction where molecule j , is surrounded by molecules i and j , while τ_{ji} represents the case of interaction where molecule i , is surrounded by molecules j and

i. Five parameters (a_{ij} , b_{ij} and α_{ij} -which is symmetrical), if temperature dependence is accounted for, are used to represent multiple isotherms for a single system using this model. b_{ij} is omitted if a single isotherm is regressed. All adjustable parameters are species-specific and independent of composition (Smith et al., 2001). It has been shown from the regression of large sets of experimental data of binary systems that values of α_{ij} typically lie within 0.20 to 0.47, therefore often this value is fixed (Walas, 2013). However, Walas (1985) recommends that α_{ij} be treated as an adjustable parameter if it improves the quality of the data fit.

2.6.1.2. The UNIQUAC (Universal Quasi-Chemical Activity Coefficient) Model

The UNIQUAC model was developed by Abrams and Prausnitz (1975) with two adjustable parameters per binary system (without temperature dependence). The model is more complex than the NRTL model but also has applicability to miscible and immiscible solutions and can incorporate parameter temperature dependence.

With the UNIQUAC model, group contribution methods are often used to estimate some pure component parameters for the model which include the component volume and surface area parameters using the methods of Bondi (1964). According to Abrams and Prausnitz (1975), vapour-liquid and liquid-liquid equilibria for both binary and multi-component systems which include polar and non-polar fluids such as hydrocarbons, ketones, esters, amines, alcohols, nitriles and water are well represented by the model. It is also applicable to binary mixtures consisting of molecules that differ greatly in size and shape (Abrams and Prausnitz, 1975).

The UNIQUAC model treats $\frac{G^E}{RT}$ as the combination of a combinatorial term that accounts for molecular size and shape differences and a residual term that accounts for molecular interactions and is given by:

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)_{\text{combinatorial}} + \left(\frac{G^E}{RT}\right)_{\text{residual}} \quad (2.102)$$

For binary systems:

$$\left(\frac{G^E}{RT}\right)_{\text{combinatorial}} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \quad (2.103)$$

$$\left(\frac{G^E}{RT}\right)_{residual} = -\sum_i q_i x_i \ln \sum_j \theta_j \tau_{ji} \quad (2.104)$$

The segment fraction ϕ_i is given as:

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (2.105)$$

The area fraction θ_j is given as:

$$\theta_j = \frac{x_j q_j}{\sum_j x_j q_j} \quad (2.106)$$

r and q are the pure component volume and area parameters respectively. These parameters are available in literature. z is the coordination number and is often set to 10.

The adjustable binary interaction parameters are given by:

$$\tau_{ji} = \exp \left(\frac{u_{ii} - u_{ji}}{RT} \right) \quad (2.107)$$

$$\tau_{ii} = \tau_{jj} = 1 \quad (2.108)$$

$(u_{ii} - u_{jj})$ and $(u_{21} - u_{22})$ are the characteristic energies and are weakly dependent on temperature (Prausnitz et al., 1999).

A common temperature dependence of the UNIQUAC adjustable parameters is given in equation 2.109:

$$\tau_{ji} = \exp \left(a_{ji} + \frac{b_{ji}}{T} \right) \quad (2.109)$$

The activity coefficient expression for UNIQUAC model takes similar form to the equation 2.102, as:

$$\ln \gamma_i = (\ln \gamma_{i,combinatorial} + \ln \gamma_{i,residual}) \quad (2.110)$$

Where

$$(\ln \gamma_i)_{\text{combinatorial}} = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (2.111)$$

$$(\ln \gamma_i)_{\text{residual}} = -q_i \ln \sum_j \theta_j \tau_{ji} + q_i - q_i \sum_k \frac{\theta_j \tau_{ij}}{\theta_k \tau_{kj}} \quad (2.112)$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \quad (2.113)$$

$$Z = 10 \quad (2.114)$$

The main shortcomings of the model are the complexity of the model equations and the need for pure component structural parameters.

2.7.Vapour Liquid Equilibrium (VLE)

In a closed system at constant temperature and pressure, a mixture of components can form two-phases to achieve a minimum Gibbs energy state. The relationship between the temperature, pressure and composition of a particular component in each phase, specifically vapour and liquid, forms the basis of the study of vapour-liquid equilibrium (VLE).

2.7.1. Vapour Liquid Equilibrium Diagrams

The most common types of phase diagrams that classify the VLE behaviour of binary systems is described by Raal and Mühlbauer (1998). Figure 2.1 shows generic examples of various behaviours commonly encountered in the process industries. This is not a comprehensive characterization. A more exhaustive characterization is provided by Gmehling et al.(Gmehling et al., 2019) Type (a), which is more commonly known as the intermediate-boiling systems, includes systems in which the boiling points at all proportions are in between the values of the pure component boiling points. Types (b) and (c) encompass systems which have homogeneous azeotropes. Type (b) systems exhibit minimum boiling homogenous azeotropes and (c) systems exhibit maximum boiling homogenous azeotropes. Type (d) includes systems with partially miscible liquid phases and a single heterogeneous azeotrope.

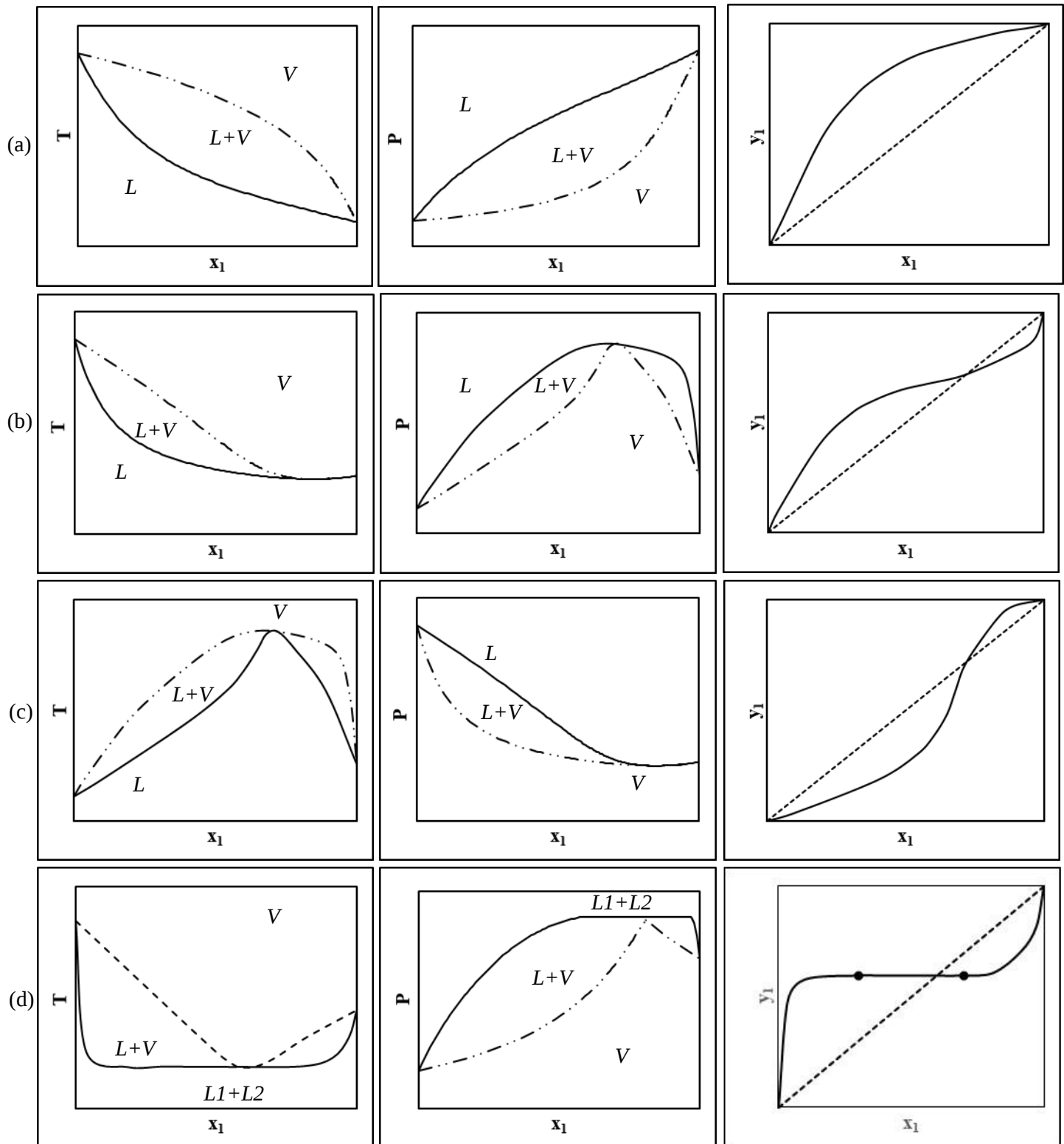


Figure 2.1. The three common types of binary phase diagrams for T - x - y , P - x - y and x - y plots (left to right): (a) intermediate-boiling; (b) minimum boiling homogeneous azeotrope; (c) maximum boiling homogeneous azeotrope; (d) heterogeneous azeotrope. (redrawn from Raal and Mühlbauer (1998)).

2.7.2. Alkane + ketone VLE behaviour

Isothermal vapour-liquid equilibrium (VLE) data for the n-hexane + butan-2-one system and the n-heptane + pentan-2-one system at 333.15 K and 363.15 K have been measured by Hanson and Van Winkle (1967) and Scheller and Rao (1973) respectively. Mixtures of n-alkanes and ketones and have been measured by Maripuri and Ratcliff (1972) to test the applicability of the Group Solution and other predictive models for the prediction of excess free energies. Isobaric vapour-liquid equilibria for the systems of butan-2-one + n-heptane have been measured by Wisniak et al. (1998).

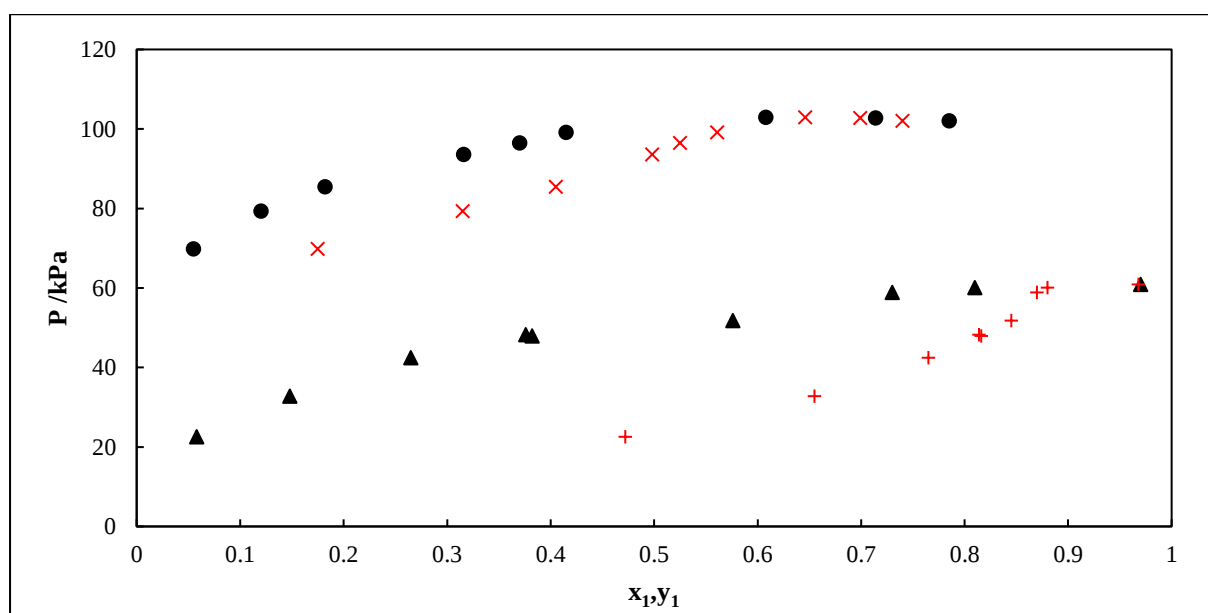


Figure 2.2. P - x - y literature data for ketone + alkane binary systems at 338.15 K by Maripuri and Ratcliff (1972). n-hexane (1) + butan-2-one (2), ●- x_1 and ×- y_1 . butan-2-one (1) + n-octane (2), ▲- x_1 and +- y_1 .

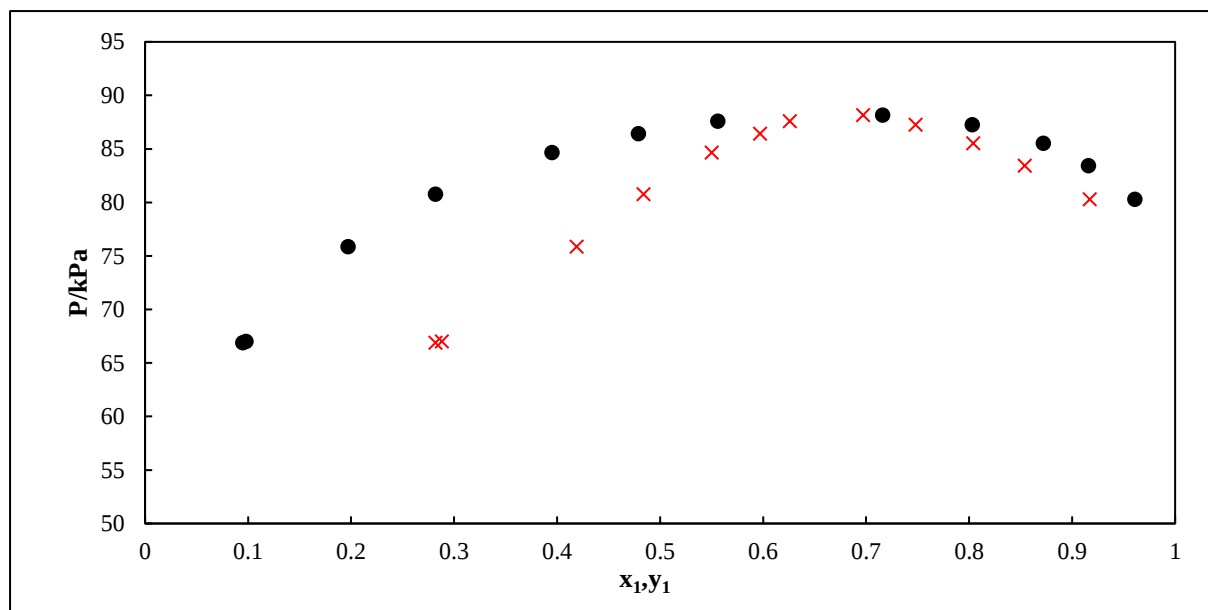


Figure 2.3. P - x - y literature data for the hexane (1) + butan-2-one (2) system at 333.15 K by Hanson and Van Winkle (1967), $\bullet$ - x_1 and $\times$ - y_1 .

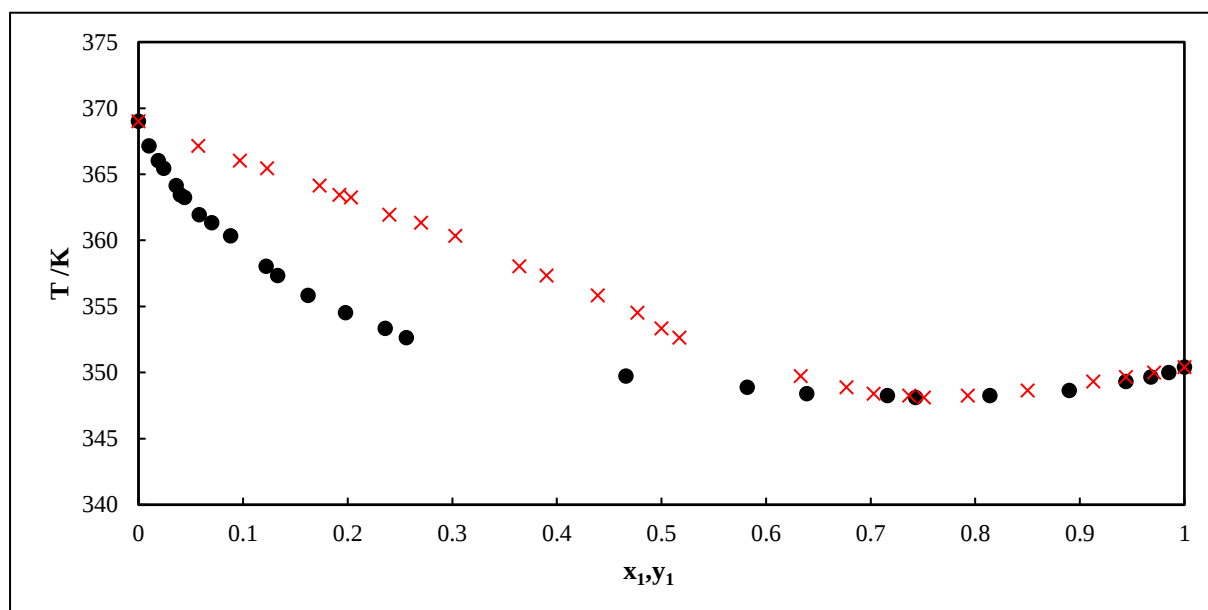


Figure 2.4. T - x - y literature data for the butan-2-one (1) + n-heptane (2) system at 94 kPa by Wisniak et al. (1998), $\bullet$ - x_1 and $\times$ - y_1 .

The n-hexane (1) + butan-2-one (2) and butan-2-one (1) + octane (2) isothermal VLE data of Maripuri and Ratcliff (1972) is shown in Figure 2.2. The n-hexane (1) + butan-2-one (2) system of Hanson and Van Winkle (1967) and butan-2-one (1) + n-heptane (2) system of Wisniak et

al. (1998) is shown in Figure 2.3 and 2.4 respectively. From these figures, it is seen that the binary systems deviate from ideal behaviour and an azeotrope is present. The type of binary phase diagram presented for these alkane-ketone systems are that shown in Figure 2.1.(a) and (b) for systems with intermediate boiling and containing a minimum boiling homogenous azeotrope. From the study by Wisniak et al. (1998), the activity coefficients of the butan-2-one (1) + n-heptane (2) system was correlated well with the Redlich and Kister (1948), Wohl (1946), Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations. The RMSD value in pressure reported using the Redlich-Kister model was 0.02 kPa. The AAD values in vapour composition for the Wohl, Wilson, NRTL and UNIQUAC models were 0.005, 0.005, 0.007 and 0.006 respectively.

2.8. The gamma-phi ($\gamma - \Phi$) formulation for vapour-liquid equilibrium

Typically, in order to represent the vapour-liquid phase behaviour of low (sub-atmospheric) to moderate pressure (100-500 kPa) systems, an equation of state is used to calculate the fugacity in solution of the vapour phase. The fugacity in solution of the liquid phase can be calculated either with an equation of state or with an activity coefficient model. The gamma-phi ($\gamma - \Phi$) approach employs an activity coefficient model to account for the liquid phase non-idealities and an equation of state to determine the fugacity coefficient in solution of the vapour and correction factor (Φ_i) which accounts for the non-idealities in the vapour phase and the Poynting correction.

The $\gamma - \Phi$ formulation of VLE is represented as follows:

$$y_i \Phi_i P = x \gamma_i P_i^{sat} \quad (2.115)$$

In order to characterize vapour-liquid equilibrium data for the entire composition and temperature range, isothermal VLE data must be processed by the $\gamma - \Phi$ formulation, by determining the fitting parameters in the activity coefficient model. The summability relation given by Barker (1953) is then used to eliminate y_i from equation 2.115, so that a calculated pressure can be determined. The fitting procedure for the $\gamma - \Phi$ formulation for a bubble point calculation is shown in Figure 2.5.

In this work, the ordinary least squares method objective function was used for the experimental isothermal VLE data regression on Aspen Plus software V10 software. The objective function considers the pressure deviation and is given by:

$$S = \sum (\delta P)^2 \quad (2.116)$$

Where the difference between the model and experimental value is commonly termed a residual and is given by the symbol δ .

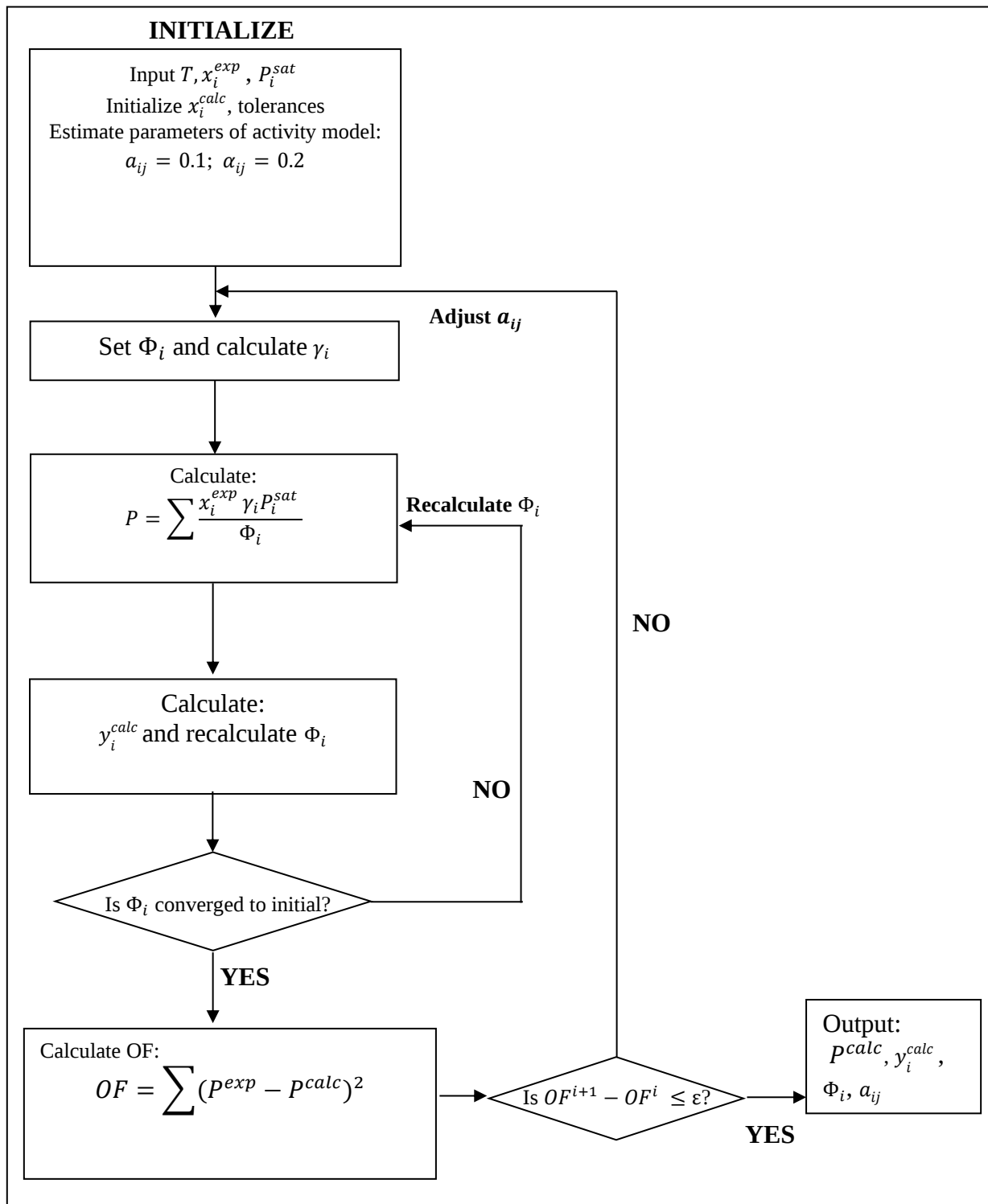


Figure 2.5. Algorithm used for the regression of isothermal VLE data using the γ - Φ method (Smith et al., 2001).

2.9. The phi-phi ($\phi - \phi$) formulation for vapour-liquid equilibrium

In the phi-phi ($\phi - \phi$) formulation for VLE regression, equations of state are used to represent non-idealities in both the liquid and the vapour phase. Commonly cubic equations of state such as those of Soave (1972) and Peng and Robinson (1976) are used. More recently statistical association fluid theory such as PC-SAFT (Gross and Sadowski, 2001) are also applied as they are used more commonly in industry. It is shown later in this work that the $\gamma - \Phi$ formulation provides a superior representation of the VLE data measured in this work, hence the $\phi - \phi$ formulation will not be discussed in further detail, however the reader is referred to Walas (2013) and Raal and Mühlbauer (1998), who provide excellent reviews of the formulation.

2.10. Determining activity coefficient at infinite dilution from VLE measurements

Methods that are generally used to determine activity coefficients at infinite dilution are gas chromatographic methods, Rayleigh distillation, ebulliometry inert gas stripping, and differential static methods. For a more detailed review of these methods, the reader is referred to the work of Raal and Mühlbauer (1998). The activity coefficient at infinite dilution can also be determined from VLE data. However, Hartwick and Howat (1995) have shown that just extrapolating binary activity coefficient curves to the end points, can result in inaccurate values of γ_i^∞ . A modification to the method of Ellis and Jonah (1962) to give acceptable values for γ_i^∞ from isothermal binary VLE data has been proposed by Maher and Smith (1979).

In the proposed method of Maher and Smith (1979) for accurately calculating infinite dilution activity coefficients from total pressure measurements the concept of the “deviation pressure”, P_D , and liquid composition, x_i , is used to get the limiting change in pressure with respect to composition, $\left(\frac{\partial P}{\partial x_1}\right)_{x_1=0}^\infty$. This method is model independent. The activity coefficient at infinite dilution can then be related to $\left(\frac{\partial P}{\partial x_1}\right)_{x_1=0}^\infty$, using physical properties of the constituents of the mixture, and the second virial coefficients determined by measurement or correlation.

The deviation pressure, P_D , is given by:

$$P_D = P - [P_2^{sat} + (P_1^{sat} - P_2^{sat}) x_1] \quad (2.117)$$

Where P is the total pressure and P_i^{sat} are the saturation pressures of component 1 and 2.

Derivation of equation 2.117 with respect to x_1 yields:

$$\frac{dP_D}{dx_1} = \frac{dP}{dx_1} - (P_1^{sat} - P_2^{sat}) \quad (2.118)$$

and applying L'Hopital's rule yields that the end points ($x_1 = 0, x_1 = 1$) are represented by:

$$\left(\frac{P_D}{x_1 x_2} \right)_{x_1=0}^{\infty} = \left(\frac{dP_D}{dx_1} \right)_{x_1=0}^{\infty} \quad (2.119)$$

$$\left(\frac{P_D}{x_1 x_2} \right)_{x_1=1}^{\infty} = - \left(\frac{dP_D}{dx_1} \right)_{x_1=1}^{\infty} \quad (2.120)$$

If a plot of $\frac{P_D}{x_1 x_2}$ vs. x_1 is linear, then the end points can be confidently determined by extrapolation of a straight line. If this plot is not linear, Maher and Smith (1979) suggest that plotting $\frac{x_1 x_2}{P_D}$ vs. x_1 , may generate a straight line. The end points are then given by:

$$\left(\frac{x_1 x_2}{P_D} \right)_{x_1=0}^{\infty} = \left[\left(\frac{dP_D}{dx_1} \right)_{x_1=0}^{\infty} \right]^{-1} \quad (2.121)$$

$$\left(\frac{x_1 x_2}{P_D} \right)_{x_1=1}^{\infty} = - \left[\left(\frac{dP_D}{dx_1} \right)_{x_1=1}^{\infty} \right]^{-1} \quad (2.122)$$

This method fails if a straight-line plot of $\frac{P_D}{x_1 x_2}$ vs. x_1 or $\frac{x_1 x_2}{P_D}$ vs. x_1 cannot be generated as extrapolation of the end points becomes inaccurate. Substituting the value of the end point from any of the equations 2.119-2.122 into equation 2.118, allows $\left(\frac{\partial P}{\partial x_1} \right)_{x_1=0}^{\infty}$ to be calculated at a

specific end point ($x_1 = 0, x_1 = 1$). $\frac{dP}{dx_1}$ can then be related to the activity coefficient at infinite dilution as shown by Raal et al. (2006) as follows:

$$\gamma_i^\infty = \varepsilon_i^\infty \frac{P_j^{sat}}{P_i^{sat}} \left[1 + \beta_j \frac{1}{P_j^{sat}} \left(\frac{dP}{dx_i} \right)_T^{x_1 \rightarrow 0} \right] \quad (2.123)$$

Where

$$\varepsilon_i^\infty = \exp \left[\frac{(B_{ii} - V_i^L)(P_j^{sat} - P_i^{sat}) + \delta_{ij} P_j^{sat}}{RT} \right] \quad (2.124)$$

$$\beta_j = 1 + P_j^{sat} \left[\frac{(B_{jj} - V_j^L)}{RT} \right] \quad (2.125)$$

And
$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2.126)$$

2.11. Thermodynamic consistency tests

The thermodynamic consistency tests are a means to determine if the VLE data obtained is consistent among the measured variables. Several tests are based on the Gibbs-Duhem relation and makes use of the concept that binary VLE has a degree of freedom of two. So, if four parameters are measured (pressure, temperature, vapour and liquid composition), then any fourth parameter can be calculated from the other three.

The Gibbs Duhem equation is the basis for thermodynamic consistency tests such as the area test and is given as:

$$\sum x_i d \ln \gamma_i = \frac{\bar{V}^E}{RT} dP - \frac{\bar{H}^E}{RT^2} dT \quad (2.127)$$

Experimental VLE data must agree with the equation above to be thermodynamically consistent. For low pressure isothermal VLE data, the area test and point test may be applied to test for consistency (Raal and Mühlbauer, 1998). Both tests must be applied since performing

the area test alone may lead to inaccurate conclusions (Narasigadu, 2006). Wisniak et al. (2017) recommend that the point test of Fredenslund et al. (1977) must always be applied to VLE data as a rigorous test, along with any additional test, such as the area test of Redlich and Kister (1948) or the infinite dilution test of Kojima et al. (1990).

2.11.1. The Area Test

The area test uses the ratio of the areas under the curves for the experimental $\ln \gamma_i$ plots for each species and is applied to the entire set of data. To satisfy the area test, the net area should be less than or equal to a tolerance percent of the total area, usually taken as 10%. This criteria is not very stringent and individual publications often impose a stricter criterion to evaluate data consistency (Van Ness, 1995).

2.11.2. The Point Test

The point test for thermodynamic consistency testing was introduced by Van Ness et al. (1973). The point test uses three of the four usually measured variables (x_i , y_i , T , P) to calculate the fourth variable, and thereafter compares it with the experimental value (Prausnitz et al., 1999). In most cases the vapour phase compositions introduce the most error (Smith et al., 2001), therefore the measured vapour compositions are used to test for the consistency of the data. The difference between the experimental vapour composition (y_{exp}) and the calculated vapour composition (y_{calc}) is found. The absolute average deviation for the point test (AAD_{point}) is then obtained and for the data to be thermodynamically consistent, the value should be less than 0.01 (Narasigadu, 2011).

The AAD_{point} is given by:

$$AAD_{\text{point}} = \frac{1}{N} \sum_{i=1}^N |\Delta y - \Delta \bar{y}| \quad (2.128)$$

Where N is number of data points, Δy is the difference between experimental and calculated data and $\Delta \bar{y}$ is the average of Δy (Narasigadu, 2011). As mentioned, in this work the point test of Fredenslund et al. (1977) was used which employed a Legendre polynomial to fit the experimental VLE data, and calculate Δy as well as δP . The tolerance for Δy was taken as

0.01, and it was insured that the deviations, Δy and δP were randomly scattered as both positive and negative deviations according to the recommendations of Wisniak et al. (2017).

2.11.3. Infinite Dilution Test

The infinite dilution test of Kojima et al. (1990) is a test for consistency observing the limiting behaviour of $G^E/(x_1x_2/RT)$ and the logarithms of the activity coefficients γ_1 and γ_2 . The test basically states that these variables must be coherent at the end points, (within a certain percentage deviation tolerance) as the mixture approaches infinite dilution. The percent deviations in both limits are calculated:

$$I_1 = 100 \left| \frac{\frac{G^E}{x_1x_2RT} - \ln \left(\frac{\gamma_1}{\gamma_2} \right)}{\ln \left(\frac{\gamma_1}{\gamma_2} \right)} \right|_{x_1=0} \quad (2.129)$$

$$I_2 = 100 \left| \frac{\frac{G^E}{x_1x_2RT} - \ln \left(\frac{\gamma_2}{\gamma_1} \right)}{\ln \left(\frac{\gamma_2}{\gamma_1} \right)} \right|_{x_2=0} \quad (2.130)$$

If $I_1 < 30$ and $I_2 < 30$, the data set passes the test; otherwise it fails.

2.12. Liquid-liquid equilibrium (LLE)

Liquid-liquid phase splitting occurs when a liquid mixture can achieve a lower Gibbs energy state by forming two liquid phases. In a closed system at constant temperature and pressure such a system will reach liquid-liquid equilibrium (LLE).

2.12.1. Binary systems

In binary systems, LLE is usually represented as a plot of T versus x_1 . The three common types of solubility curves (or binodal curves) are shown in Figure 2.6. Figure 2.6 (a) is a common type of behaviour and represents a system exhibiting an upper critical solution temperature (UCST) or T_U . At temperatures above T_U , a single liquid phase occurs. (b) is another common type of behaviour and represents a system exhibiting a lower critical solution temperature (LCST) or T_L . At temperatures below T_L , a single liquid phase occurs. (c) shows an “island”. This behaviour is not commonly encountered in common solvent mixtures and possesses a

UCST and an LCST. For temperatures between T_L and T_U , LLE is possible in certain composition ranges. For $T < T_L$ and $T > T_U$, a single liquid phase exists.

If the freezing point of the mixture is higher than the hypothetical lower critical solution temperature (LCST), then the system will usually freeze before homogenizing. If the boiling point of the mixture is lower than the hypothetical upper critical solution temperature (UCST), then the solution will boil before homogenizing.

Points A and B represent the corresponding equilibrium points (compositions) at any specific temperature. That means that if a mixture is prepared with an overall composition between A and B, and brought to an equilibrium temperature T , then the system will split into two phases with compositions of A and B for component 1. The line joining A and B is called a tie-line.

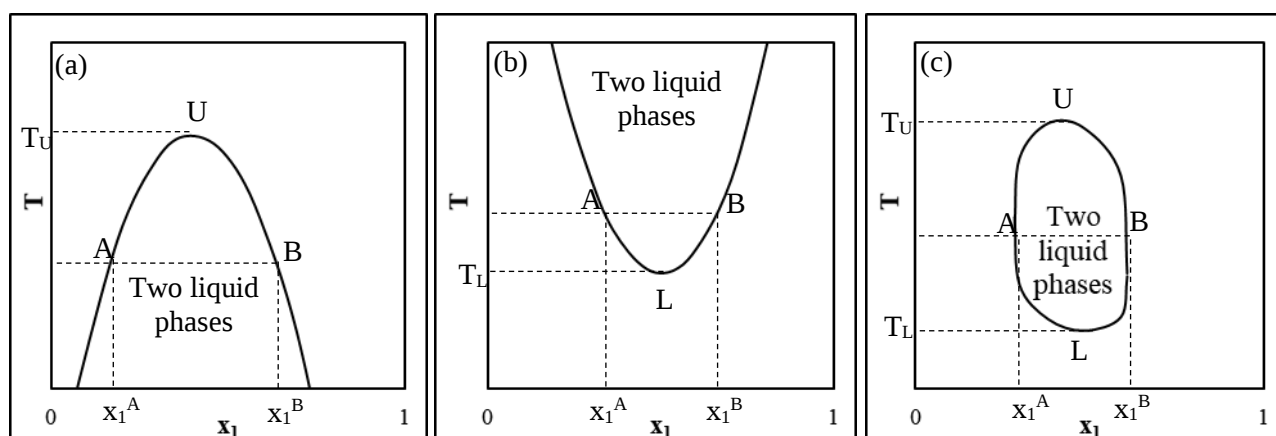


Figure 2.6. Common types of constant pressure binary LLE diagrams: (a) “a convex curve” with upper critical solution temperature, (b) “a concave curve” with lower critical solution temperature and (c) “an island curve”, (Classifications re-drawn from Smith et al. (2001)).

The T - x_1 diagram for the methanol (1) + n-hexane (2) binary system reported by Blanco and Ortega (1996) and Orge et al. (1997) is shown in Figure 2.7. The type of behaviour observed is a “convex curve” with upper critical solution temperature as shown in 2.6 (a). In the study by Orge et al. (1997), the UNIFAC-Dortmund group contribution method was applied to predict LLE in the system and gave good agreement at high methanol composition.

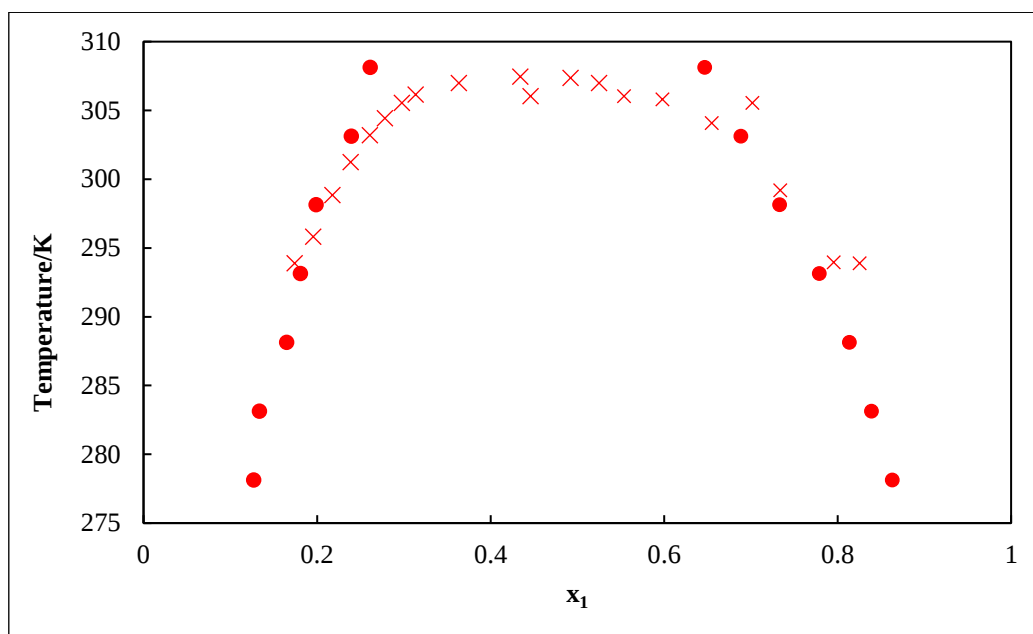


Figure 2.7. T - x_1 literature data for the methanol (1) + n-hexane (2) binary system at 0.1MPa. $\times$ - x_1 of (Blanco and Ortega, 1996), $\bullet$ - x_1 of (Orge et al., 1997).

2.12.2. Ternary systems

Data for ternary LLE are usually represented on a triangular phase diagram as shown in Figure 2.8. Each pure component is represented by each vertex of the triangle. The area above the binodal curve seen in Figure 2.8 is the single liquid-phase region and the area within the curve is the two-liquid phase region. The equilibrium compositions of the two phases can be determined experimentally which is then used for the construction of the tie lines of the two-phase region. The point at which the compositions of both phases are equal is known as the plait point.

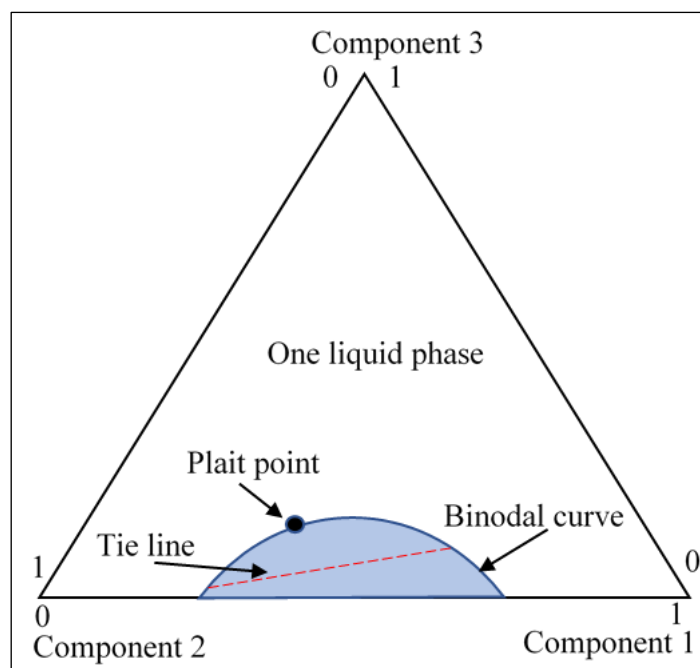


Figure 2.8. Graphical representation of ternary liquid-liquid equilibrium data using a triangular phase diagram (re-drawn from Novák et al. (1987)).

The two main types of ternary systems are type I and type II. A type I system is a system which contains one binary immiscible pair and two binary miscible pairs. A generic example of a type I system is shown in Figure 2.9 (a). Type one systems are generally the most commonly encountered in industry. In a type II system, there are two binary pairs that are partially miscible and one binary pair that is completely miscible. A generic example of a type II system is shown in Figure 2.9 (b).

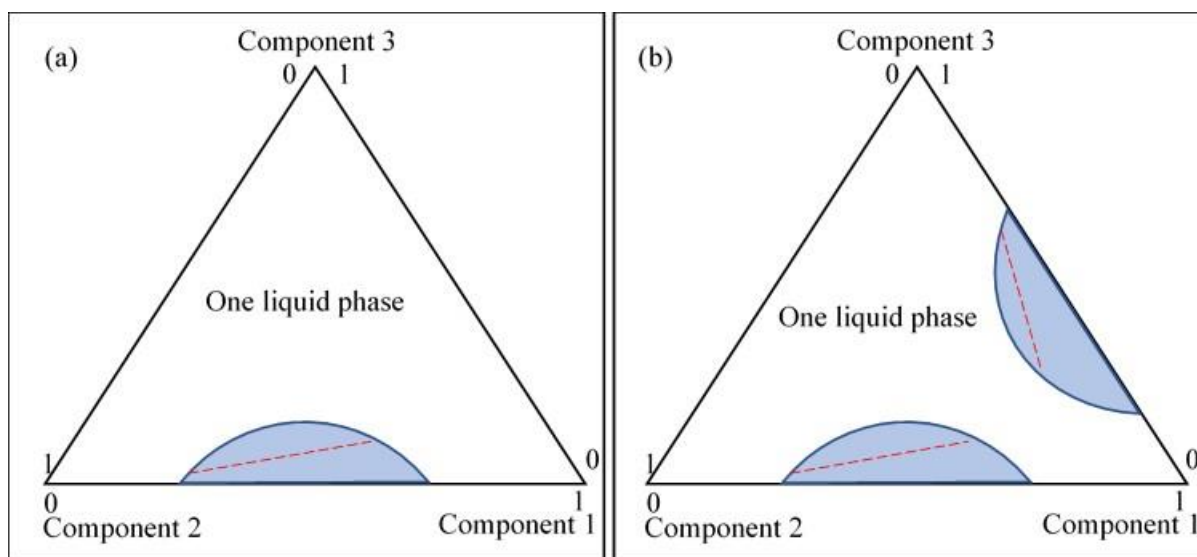


Figure 2.9. Types of ternary systems with two-phase regions (Novák et al. (1987)).

Literature data for the acetone (1) + methanol (2) + n-octane (3) ternary system at 278.15K , 288.15 K and 298.15K measured by Marino et al. (2000) is shown in Figure 2.10. The tie line data were correlated with the UNIQUAC model, and good accuracy has been achieved for all cases with temperature dependence parameters. The root mean square deviations reported were between 0.003 and 0.008. From Figure 2.10 a type I system is observed and the size of the two-phase region decreases with an increase in temperature.

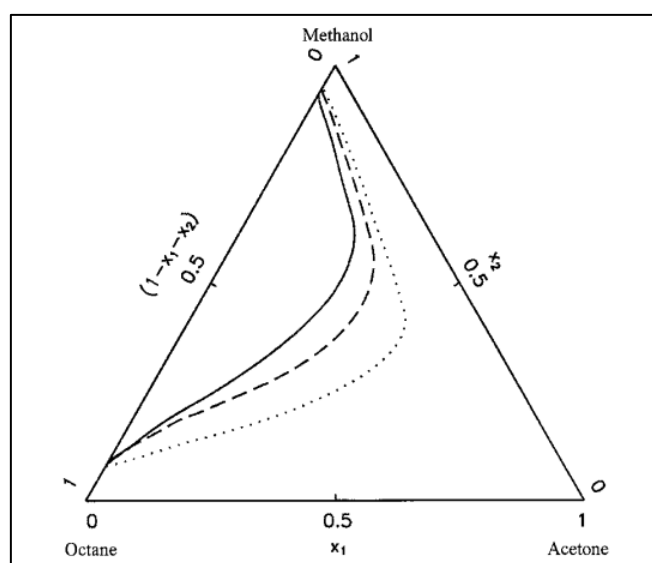


Figure 2.10. Ternary LLE literature data of Marino et al. (2000) for the acetone (1) + methanol (2) + octane (3), (···) 278.15 K; (---) 288.15 K; (-) 298.15 K.

2.13. Theoretical treatment of liquid-liquid equilibrium

A stable system is a system that has a minimum Gibbs energy at a fixed temperature and pressure. As mentioned previously, a solution can form two liquid phases if it results in the mixture having a lower Gibbs energy. The Gibbs energy change of mixing (ΔG^{mix}) is defined as:

$$\Delta G^{mix} = G - \sum x_i G_i \quad (2.131)$$

where G refers to the Gibbs energy of the mixture and G_i refers to the Gibbs energy of the pure components.

Figure 2.11 shows a generic curve of Gibbs energy change of mixing versus composition at constant temperature and pressure. Point a represents the Gibbs energy change of mixing at composition x_1 . It is possible to achieve a lower Gibbs energy to point (b) which lies on a tangent to the curve at the minimum values of ΔG^{mix} . The mixture is at equilibrium when the mixture achieves the Gibbs energy at point (b) because this is the lowest possible Gibbs energy that the mixture can achieve at constant temperature, pressure and overall composition of x_1 . The mixture will then split into two phases with compositions x_1^A and x_1^B which are tangential points on the curve. This is only applicable if the curves for Gibbs energy are in part concave downwards (Prausnitz et al., 1999).

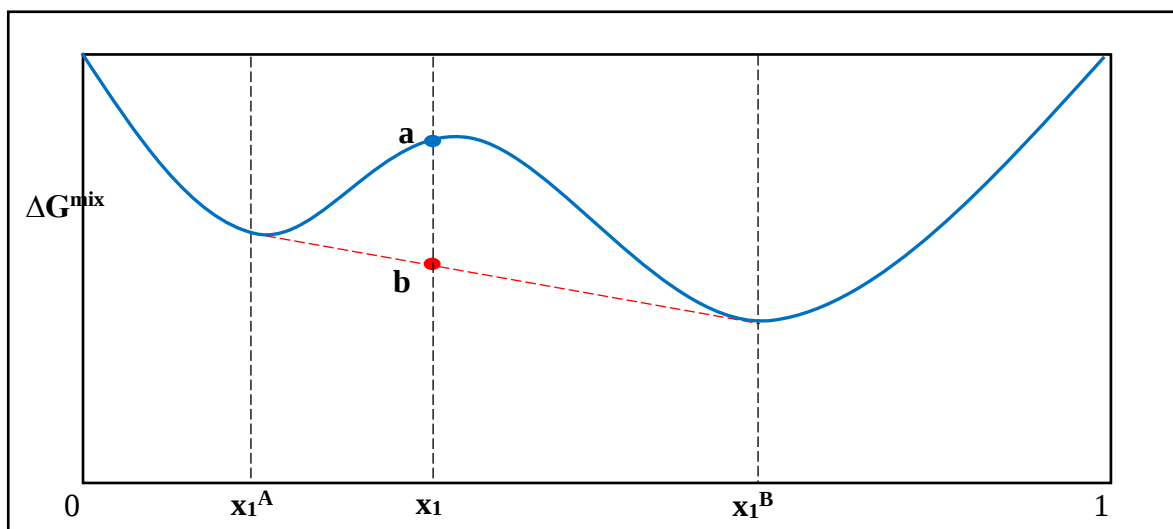


Figure 2.11. Molar Gibbs energy change of mixing for a partially miscible binary system (re-drawn from Prausnitz et al., 1999).

In the mathematical interpretation of Figure 2.11, ΔG^{mix} and its first and second derivatives are continuous functions of x_1 . In an unstable system (one with two liquid-phases) the second derivative of ΔG^{mix} must be negative in the immiscible region.

For a binary system:

$$\frac{d^2 \Delta G^{mix}}{dx_1^2} < 0 \quad (2.132)$$

Equally, in terms of Gibbs excess energy (G^E), for stability:

$$\frac{d^2 \left(\frac{G^E}{RT} \right)}{dx_1^2} < \frac{1}{x_1 x_2} \quad (2.133)$$

From the criterion of phase equilibrium for two liquid phases α and β :

$$\hat{f}_i^{(\alpha)} = \hat{f}_i^{(\beta)} \dots\dots\dots (i=1, 2, \dots N) \quad (2.4)$$

The activity coefficient concept was introduced to account for deviation from ideality (i.e., an ideal solution) with respect to the liquid phase during phase equilibrium calculations.

The fugacity in solution for a component i is defined by:

$$\hat{f}_i = x_i \hat{f}_i^o \gamma_i \quad (2.134)$$

Generally, the effect of pressure on the fugacity in solution of liquids is only significant at high pressures or near the critical point, hence at low to moderate pressures, the effect of pressure on the activity coefficient is usually ignored.

Therefore, at low to moderate pressure for two liquid phases from equation 2.131 and 2.134:

$$x_i^{(\alpha)} \gamma_i^{(\alpha)} \hat{f}_i^{0(\alpha)} = x_i^{(\beta)} \gamma_i^{(\beta)} \hat{f}_i^{0(\beta)} \quad (2.135)$$

If the reference state is a pure component, its fugacity does not depend on phase α and β , hence:

$$\hat{f}_i^{0(\alpha)} = \hat{f}_i^{0(\beta)} \quad (2.136)$$

Therefore, the fundamental relation of LLE is obtained

$$x_i^{(\alpha)} \gamma_i^{(\alpha)} = x_i^{(\beta)} \gamma_i^{(\beta)} \quad (2.137)$$

From equation 2.137, the only contribution to an LLE calculation is the phase composition and activity coefficient which is in-turn a function of temperature and composition.

2.14. Tie-line correlation

The binary and ternary LLE data were fit to the NRTL and UNIQUAC activity coefficient models. A fixed α_{12} parameter was used in the NRTL model, as suggested by Raal and Mühlbauer (1998) to reduce the degree of freedom of the fitting equations. The model parameters are determined by minimizing an objective function describing the deviations in composition for each component in each phase for a specific pressure and temperature. This is suggested by Novák et al. (1987):

$$OF = \left(\frac{\sum_1^N \sum_\alpha \sum_i^2 (x_i^{\alpha exp} - x_i^{\alpha calc})^2}{N} \right)^{1/2} \quad (2.138)$$

where x_i is the liquid phase mole fraction, N is the number of experimental points, and π and α are the two phases.

The algorithm proposed by Walas (2013) was used to obtain activity coefficient model parameters. This is shown in Figure 2.12.

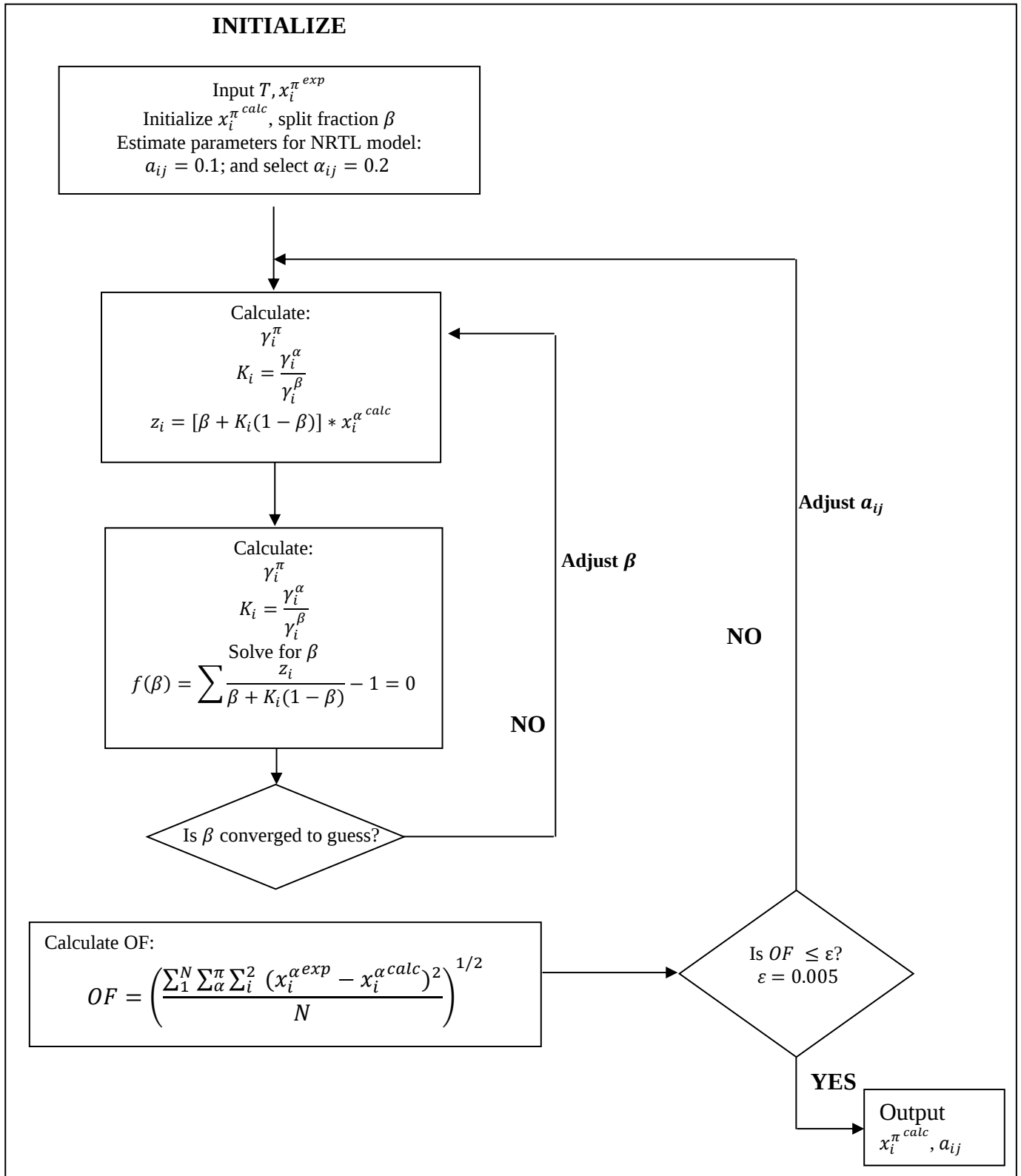


Figure 2.12. LLE tie-line fitting algorithm proposed by Walas (2013).

2.15. Gasoline Blending and Blending Limits

With the understanding of the phase behaviour from the VLE and LLE plots, it becomes easier to relate and interpret the constraints of these species in mixtures. Semi-finished products from refining processes often need to be blended to meet the specifications of the required end-products. The main aim of product blending is to find the best way of mixing different intermediate products from the refinery together with additives in order to adjust the product specifications (Fahim et al., 2010). A refinery has several different hydrocarbon streams to consider as blend stocks. Different grades of gasoline are produced by blending a number of different components that include fluid catalytic cracking gasoline, alkylate, reformate and oxygenated additives. Components may be blended to simultaneously meet many different quality specifications, such as vapour pressure, initial, intermediate, and final boiling points, sulphur content, colour, stability, aromatics content, olefin content, octane number (ON) for several different portions of the blend, and other local governmental or market restrictions (Curley, 2011; Fahim et al., 2010). Octane number is a number that is used to measure the antiknock properties of a liquid motor fuel (such as gasoline) with a higher number indicating a smaller likelihood of knocking (Speight, 2019). Gasoline, jet fuels, heating oils, and diesel fuels are key refinery products produced by product blending processes (Fahim et al., 2010).

The components in gasoline need to have a high-octane number in order to prevent autoignition of fuel during compression (Parkash, 2009). The ON of a hydrocarbon is a function of its chemical composition (Parkash, 2009). Hydrocarbons with a high percentage of straight chain paraffins have a very low ON (Parkash, 2009). Branched chain normal paraffins, aromatics and olefins have high octane numbers (Parkash, 2009). Straight run naphtha from crude distillation has the correct boiling range for gasoline blending but it has a low ON between 65 to 70 due to the high percentage of n-paraffins (Parkash, 2009). The target ON of 85 to 95 of gasoline depends on the gasoline specifications in the region of usage. Product qualities are predicted through correlations that depend on the quantities and the properties of the blended components. Basic blending equations used in product blending can be found in Appendix F. The ON for gasoline is correlated based on aromatics and olefin content (Fahim et al., 2010). Oxygenates blending consists of the addition oxygen to fuel via oxygen-bearing compounds such as, methanol, ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether, pentan-2-one, 4-methylpentan-2-one, which reduces the amount of carbon monoxide and unburned

hydrocarbons in exhaust gases and reduce knocking (Parkash, 2009). Reformulated gasoline (RFG) regulations allow gasoline formulations with oxygenates to contain 0 to 3.7 wt % oxygen. Adding oxygenates to gasoline in the form of alcohols such as ethanol is one of the most effective ways to reduce aromatics and distillation temperature (Parkash, 2009). Due to its low biodegradability and concerns over ground and surface water contamination MTBE is no longer favoured in gasoline. Possible replacements include MPK and MIBK.

The use of alternative fuels such as biofuels contributes to the lowering of the carbon footprint of the internal combustion engine (Niculescu et al., 2019). Biodiesel, bioethanol, and biomethanol are amongst the most prominent alternative fuels to be used in mixtures/blends with fossil fuels (Niculescu et al., 2019). Alcohols such as methanol and ethanol are added in biodiesel–diesel blends due to their miscibility with pure biodiesel (Niculescu et al., 2019). Alcohols improve the physio-chemical properties of biodiesel–diesel blends, which result in improved internal combustion engines operation. Pure methanol cannot be used directly in diesel engines that are unmodified because it will require spark or ignition assistance or a fuel additive. However, use of diesel blended with up to 20% of methanol by volume requires only minor engine modifications (Lin and Chao, 2002). Methanol effectively improves the octane of gasoline without increasing its already high aromatics and olefin content (Methanol Institute, 2016). High amounts aromatics can contribute to performance problems in some vehicles and cause higher exhaust emissions. Unlike aromatics, the use of methanol for improving ON in gasoline has been shown to have environmental benefits, as methanol blends reduce exhaust emissions from most vehicles (Methanol Institute, 2016). It has been reported that using blended fuel results in better performance than conventional fuel (Liu et al., 2007).

Challenges to the Blending Process

Computer-controlled in-line blending is used by most refiners for blending gasoline and distillates (Weiland, 1969). Inventories of blending stocks, together with cost and physical property data are maintained in a database. Estimating final blend properties from the components can be quite complex due to a lot of the properties of blend components, such as octane number, being non-linear. When a certain volume of given quality product is specified, the computer is usually programmed to use linear programming models to optimize the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost. To match the optimized recipes for the products, accurate measurement is required. Inaccurate thermodynamic property measurement can result in

products that do not meet specification, necessitating downgrading, or that requiring doctoring of the blend in the final tank, which costs time and money.

Blending limits

Due to these challenges, blending limits must be well characterized in order to achieve product recipe targets. Figure 2.13 shows the homogenous blending limit and blending region of a ternary mixture. The binodal curve separates the single liquid-phase region the two-liquid phase region which is the area within the curve. The LLE binodal curve represents the blending limit of the mixture. The single liquid-phase region which is the area outside of the binodal curve in the ternary diagram is the blending region. These are the compositions that can be mixed for a homogenous mixture.

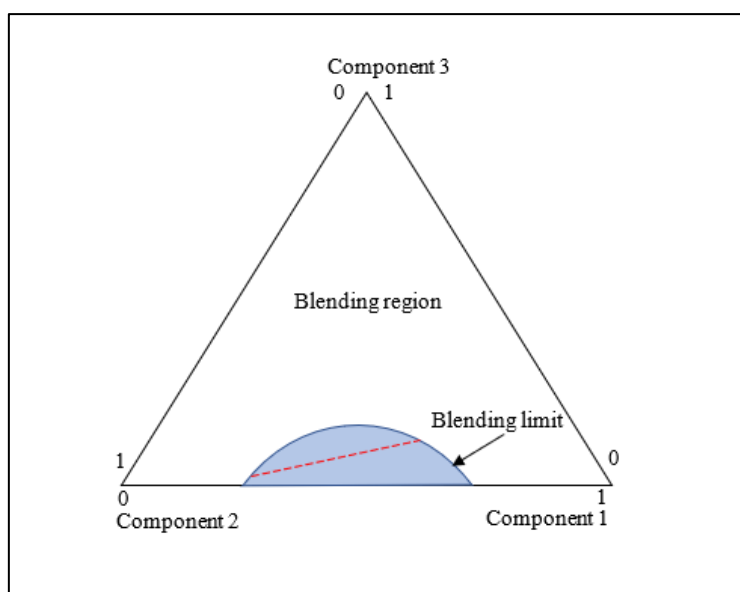


Figure 2.13. Graphical representation of a triangular phase diagram showing blending region for a mixture.

This literature review presents the theoretical aspects of vapour-liquid and liquid-liquid phase equilibrium data. The methods proposed for the evaluation of the fugacity and activity coefficients are examined. Analysis, regression, and correlation of the experimental VLE and LLE data are also discussed. This includes a review of the γ - Φ and ϕ - ϕ regression approach of VLE and tie-line correlation by minimization of the objective function using nonlinear least-squares for the LLE data. The NRTL and UNIQUAC activity coefficient models used to account for the non-ideality of the liquid phase in the VLE data using the γ - Φ approach and to correlate the experimental tie lines for the LLE data is outlined, along with the Hayden and O'Connell correlation in the virial equation of state which is used to account for the vapour phase non-ideality in this work. The Peng-Robinson and Perturbed-Chain Statistical Associating Fluid Theory equations of state used to model the VLE data by the ϕ - ϕ approach is also outlined. The most common types of phase diagrams that classify the VLE behaviour of binary systems and some common types of binary and ternary LLE diagrams are highlighted, along with literature data depicting alkane + ketone phase behaviour. Ketone-alkane systems are known to be azeotropic with a maximum boiling azeotrope and these systems form azeotropes with methanol. From the literature data, the LLE will most likely be a type I LLE system with upper critical solution temperature. Thermodynamic consistency tests used for VLE data and equations to evaluate the linearity of the ternary LLE data regarding the correspondence of the measured tie-line data is also included. This chapter also includes a discussion on gasoline blending and blending limits. Phase equilibrium data is necessary for any rigorous separation process design to assess the separation limits or potential, and also to characterize the limits of blending procedures.

CHAPTER THREE

Review of Experimental Apparatus and techniques

This chapter begins with a brief review of the techniques and equipment used for low pressure vapour-liquid and liquid-liquid equilibrium measurements. This is followed by a description of the equipment used in this work: a replica of a modified low pressure vapour-liquid equilibrium still of Raal and Mühlbauer (1998) originally commissioned by Joseph et al. (2001) and a modification of the LLE apparatus of Raal and Brouckaert (1992) commissioned initially by Ndlovu (2005), as well as temperature, pressure and composition measurement and equilibration procedure used.

3.1.Vapour-liquid equilibrium (VLE)

Vapour-liquid equilibrium measurements are conducted using two main methods, specifically static methods and dynamic (circulation) methods. In the static method, the equipment is filled with a thoroughly degassed liquid mixture which is then agitated mechanically until equilibrium is established between the liquid and its vapour. For a more detailed review of static equipment experimental methods, the reader is referred to Hála et al. (1967), Malanowski (1982), Marsh (1989), Raal and Mühlbauer (1994) and Raal and Mühlbauer (1998). In the dynamic method, there is circulation of one or both phases (vapour and liquid) through the equilibrium chamber. The dynamic method is discussed further in this chapter as this was the technique adopted in this study.

3.1.1. VLE measurement by the dynamic method

In the dynamic method, a liquid mixture is charged into a distilling chamber and brought to a boil. The vapour and liquid mixture is separated in the equilibrium chamber and the vapour phase is condensed and returned to the boiling chamber (Uusi-Kyyny, 2004). The liquid phase formed in the equilibrium chamber can also be circulated. The composition of the boiling liquid and the vapour change with time until equilibrium is reached and the temperature and pressure remain constant. The dynamic method can be conducted under isobaric or isothermal conditions. Measurements of temperature, pressure, liquid and vapour compositions are recorded when the system is in phase equilibrium. This method is also known as the circulation

method and early designs include the stills of Othmer (1928), Gillespie (1946) and Yerazunis et al. (1964). In this work, a replica of a modified version of the still of Raal and Mühlbauer (1998) commissioned initially by Joseph et al. (2001) and run in the manual mode was used for VLE measurements.

3.1.1.1. The VLE still of Othmer

The Othmer (1928) still which was designed for the recirculation of the vapour phase only was amongst the earliest types of dynamic still. In this equipment the binary mixture enters the reboiler. The mixture is brought to a boil using an electric heater. The vapour generated from the boiling liquid passes through an elliptical aperture and is sent to a condenser. The condensate is collected in a receiver for analysis, and the excess condensate is returned to the boiling flask. There are sampling points for both the vapour and liquid phases.

Some problems with this design which caused errors in measurements included:

- The temperature probe was not in contact with both equilibrium phases therefore temperature measurement was not reliable.
- There was a possibility of partial condensation of the equilibrium vapour on the wall of the boiling flask which would change the equilibrium composition.
- The condensate receiver was too large in proportion to the reboiler. The mixture in the boiling chamber was not stirred and therefore there may have been some composition gradients.

3.1.1.2. The VLE still of Gillespie

The modification by Gillespie (1946) included the incorporation of the Cottrell pump to assist the achievement of phase equilibrium. A Cottrell pump was used to aid circulation, which allowed more accurate temperature measurements (Cottrell, 1919). However, as with the Othmer apparatus, equilibrium must be accomplished in a single pass. Repeated circulation would not result in a closer approach to equilibrium than that of a single pass at steady state. Widely used dynamic stills are usually variations and improvements of the original Gillespie still (Raal and Mühlbauer, 1998).

Some drawbacks of this still included:

- The still operation is disturbed during the removal of the liquid and vapour samples, which affects the equilibrium compositions.
- Withdrawn liquid samples from the boiling chamber is not in equilibrium with the recirculating vapour.
- The Cottrell tube itself is not sufficient for the attainment of equilibrium as mass transfer is limited due to small contact times and interfacial areas.
- The time taken to for equilibrium to be reached is very long.
- There are no stirrers in the reboiler and condensate receiver which inhibits homogenization of the sampled vapour phase.

3.1.1.3. The VLE still of Yerazunis et al.

In the apparatus of Yerazunis et al. (1964), dynamic equilibrium is achieved when vapour and liquid is forced downward co-currently through a short packed adiabatic chamber. The packed column design was earlier used by Heertjies (1960). This apparatus can be computer controlled to give either isobaric or isothermal data. The temperature is measured near the bottom of the packing. Important features include the vacuum-jacketed Cottrell tube and the vapour lagging of the equilibrium chamber, in addition to a vacuum outer jacket, to ensure complete adiabaticity. Thermodynamically consistent data have been obtained with the equipment, operated by PC in either isobaric or isothermal mode (Raal and Ramjugernath, 2005).

3.1.1.4. The VLE apparatus of Joseph

In this work, the dynamic method was employed to obtain VLE data by use of a replica of a modified low pressure vapour-liquid equilibrium still of Raal and Mühlbauer (1998) originally commissioned by Joseph et al. (2001). The details of this equipment used, and equilibration procedure will be discussed the sections which follow.

3.1.1.5. Description of the dynamic VLE still

Based on the still of Yerazunis et al. (1964), Raal and Mühlbauer designed a robust equilibrium still to minimize some of the limitations on earlier designs in the literature. In this work, a replica of this modified low-pressure vapour-liquid equilibrium still was used to measure the VLE data. The apparatus is shown in Figure 3.1, with the experimental layout shown in Figure 3.2. The design of the still included a vacuum jacketed Cottrell tube and a packed equilibrium

chamber. The purpose of the vacuum jacket is to prevent the partial condensation of the vapour phase in the equilibrium region and to reduce heat losses to the environment. The packing in the equilibrium chamber consists of stainless-steel wire mesh cylinders. This together with the Cottrell tube facilitate the system to reach equilibrium very quickly, with the aim of a single pass. The packed equilibrium chamber also increases the vapour-liquid mass transfer through interfacial expansion and fresh surface creation (Joseph et al., 2001).

The boiling chamber is equipped with both external and internal heaters. The main heating source is the internal heater and allows for rapid and even boiling. For measurements, the voltage to the internal cartridge heater is controlled manually. This is used to establish the region of phase equilibrium as the system maintains a plateau region between heat input and temperature when just out of the two-phase region. A slight excess of heat is required to overcome the pressure drop in the Cottrell pump (Kneisl et al., 1989). Trial and error was used to ensure the true plateau region was determined. The external heater compensates for heat losses to the environment. Throughout the experiment, the voltage on the external cartridge heater is usually fixed.

The magnetic stirrers are used to minimize temperature and concentration gradients in the liquid collection points within the still. The magnets attract the stirrer bars, which directly mixes the fluid inside the still. The size of the stirrer bars used is important to ensure proper stirring of the fluid, and are adjusted for viscosity and density, to maintain precision. There was constant stirring in both the boiling chamber and the condensate receiver during operation. The stirrer in the boiling chamber also ensures proper mixing of the recirculated vapour phase with the boiling liquid (Raal and Mühlbauer, 1998).

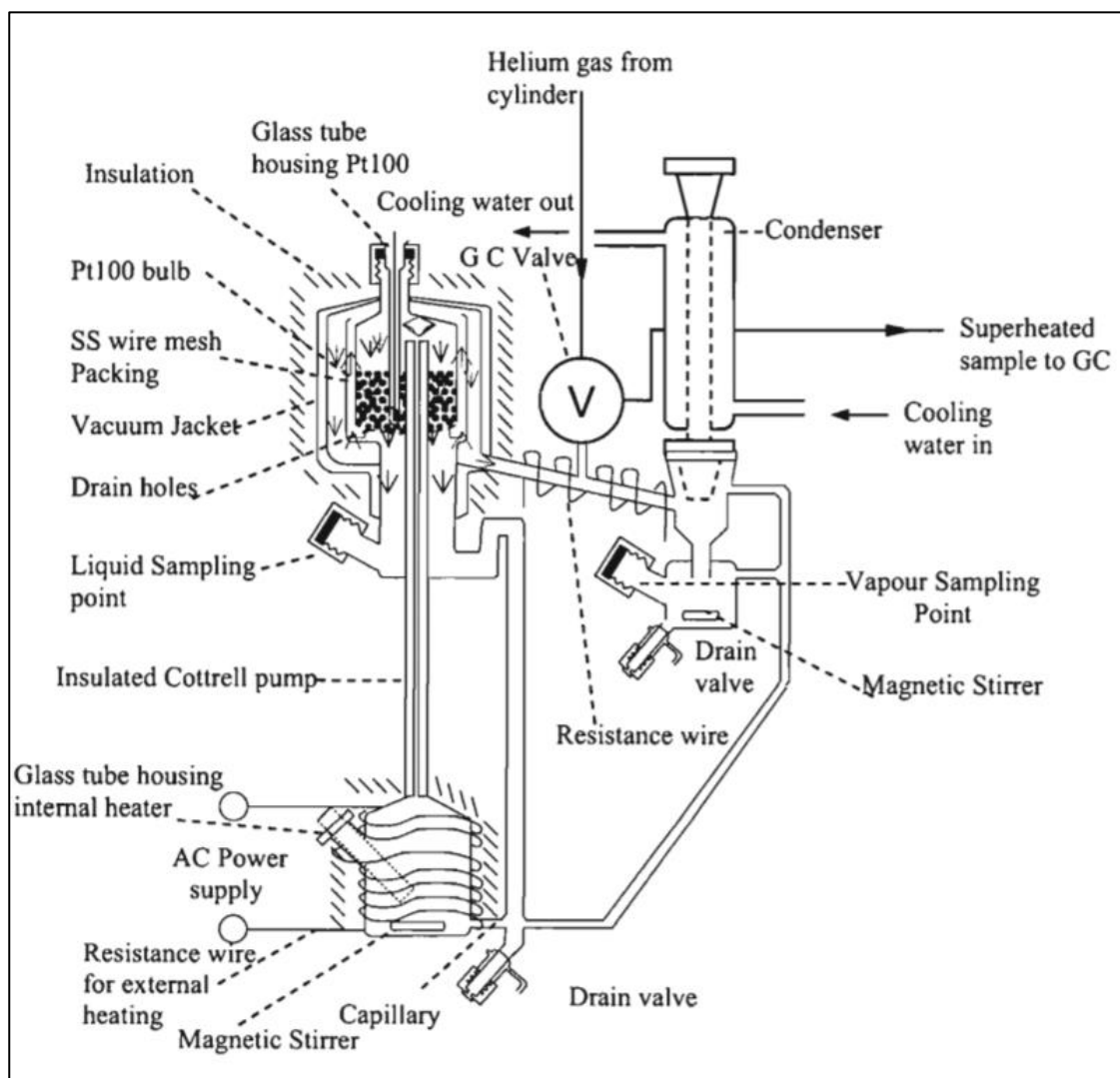


Figure 3.1. Schematic of the apparatus of Joseph et al. (2001) used in this work as shown in (Ndlovu, 2005).

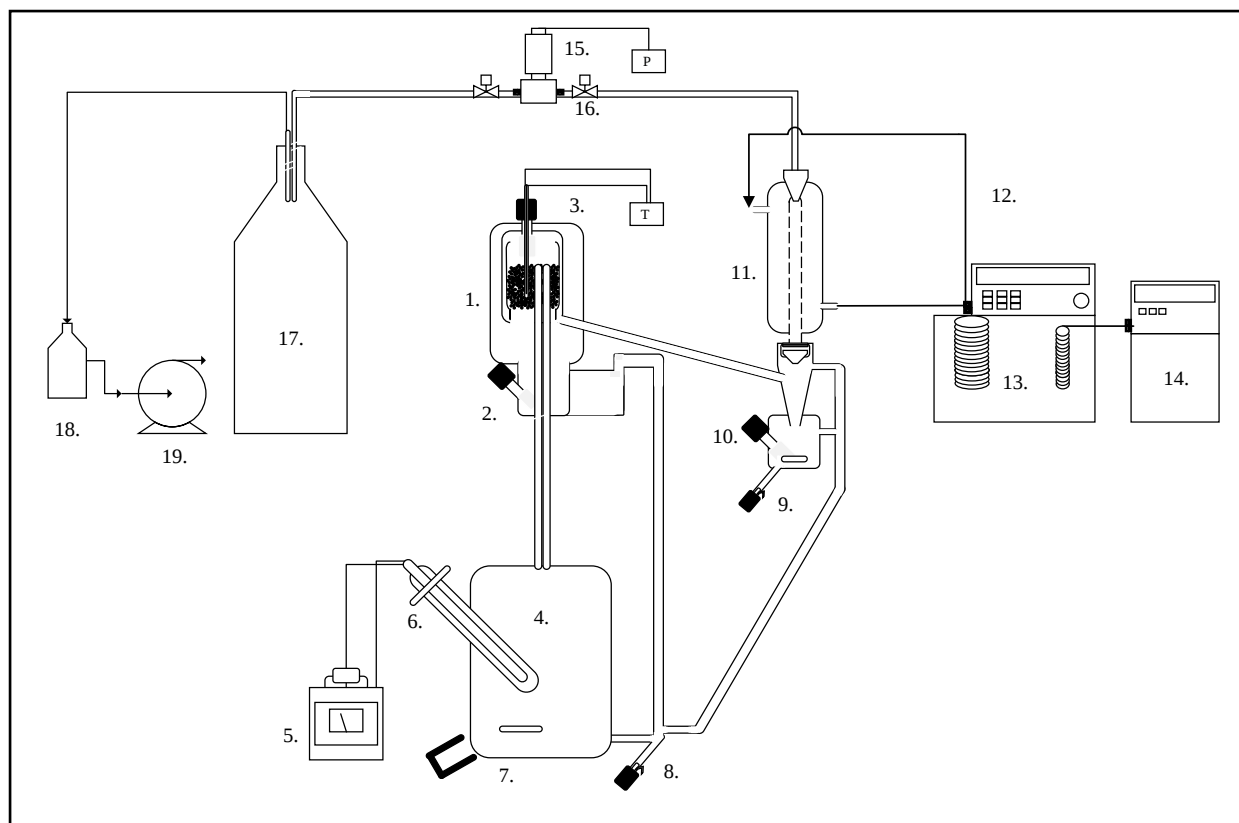


Figure 3.2. Layout of the apparatus of Joseph et al. (2001) used in this work (extracted from (Mavalal et al., 2019)).

1-Equilibrium chamber. 2-Liquid sampling port. 3-Temperature measurement. 4-Lagged boiling chamber. 5- Variable heat supply to boiler. 6- Heater cartridge and sleeve. 7- Magnetic stirrer and bead. 8- Boiler drain valve. 9- Condensate drain valve. 10- Vapor condensate sampling point. 11- Condenser. 12- Coolant line to condenser. 13. Coolant bath and controller. 14- Chiller. 15- Pressure measurement. 16. Isolation valves. 17- Ballast tank. 18. Cold trap. 19. Vacuum pump.

3.1.2. Calibrations and equilibration procedure

The calibrations for temperature, pressure and composition were performed using standard procedures, described below. The calibration plots are presented in Appendix A Figures A-1 to A-24.

3.1.2.1. Composition measurement and calibration

Phase composition analysis was conducted by gas chromatography by the use of a Shimadzu 2014 Gas Chromatograph. The analysis was carried out using a thermal conductivity detector (TCD) with helium as the carrier gas. A CRS Porapak Q 80/100 column was used as it was found to be most suited for the systems considered in this work. The stainless-steel packed column has a length of 4-m and an inner diameter of 2-mm with the maximum allowable temperature of the column being 523 K. The choice of this column was based on its ability to give good separation of the components and produce sharp and reproducible peaks with the selected conditions of 513.15 K for the injector, column and detector temperatures, and a flow rate of 30 ml/min for the carrier gas. Calibration was done on the gas chromatograph TCD by analysing peak areas of mixtures of synthesized composition according to the area ratio method of Raal and Mühlbauer (1998). These calibrations were then used to obtain the compositions of the analysed phase samples from the VLE measurements. The standard combined uncertainty in composition was 0.005. All uncertainties were calculated according to the procedures by NIST JCGM (2008). These are detailed in Appendix B.

3.1.2.2. Temperature measurement and calibration

A Pt-100 class-A temperature sensor was used to measure the equilibrium temperature. The signal from the temperature sensor was interpreted by an ABB F080 Controller and displayed. Calibrations for temperature were conducted externally by removing the temperature probe from the still and calibrating against a temperature standard (WIKA CTB 9100 temperature standard) with reported uncertainty of 0.05 K. The standard combined uncertainty of the temperature measurement for VLE was calculated to be 0.1 K.

3.1.2.3. Pressure measurement, control and calibration

A WIKA P-10 pressure transmitter was used to monitor the pressure of the system. The signal from the transducer was interpreted by an ABB F080 controller and displayed. Pressure calibration was conducted *in situ* using a high-purity solvent whose vapour pressure is well studied in the literature. The standard combined uncertainty of the pressure measurement was calculated to be approximately 0.1 kPa from calibration. The vacuum pump was connected through a ballast tank to the still which was used to stabilize the pressure of the system. The pressure of the system was controlled by using two solenoid valves connected to vacuum and the atmosphere.

3.1.2.4. Equilibration procedure

Prior to use, the equipment was tested for any major leaks by inducing vacuum and monitoring the vacuum hold. If no major leaks were present, the equipment was cleaned by circulating acetone for several minutes. The acetone was drained, and the residual was boiled off and the still evacuated. A comprehensive leak test was then conducted observing any leak rate over time. Any leaks were then attended to by replacing seals or tightening parts etc. The components were injected into the still through the liquid or vapour sampling point and entered the reboiler. In the boiling chamber, the mixture was brought to a boil which resulted in the vapour-liquid mixture. The thermal lift pump in the vacuum jacketed Cottrell tube helps the mixture move upward to the equilibrium chamber. In the equilibrium chamber, both the phases are separated. The movement of the vapour around the equilibrium chamber allows for thermal lagging of the chamber. The vapour was condensed and collected in the condensate receiver and the liquid flowed through the holes at the bottom of the equilibrium chamber. The equilibrium mixture then moved down through the small holes at the bottom of the equilibrium chamber and flowed over a mixing spiral. It flowed through a liquid trap and then entered the boiling chamber. A gas-tight 1 μ l GC syringe was used to remove the liquid and vapour samples without disturbing the equilibrium. Usually, 4-5 samples of each phase are taken to ensure repeatability. After use, the stirrers were switched off and the internal and external heaters were both slowly decreased to zero. The pump was switched off, the valve at the bottom of the ballast tank was opened and the valve to the still was then closed. The cold finger and controller were then switched off. After each system is measured, the still was drained to remove the chemicals. The still was then cleaned with acetone by following the discussed cleaning procedure.

3.2. Liquid-liquid equilibrium (LLE)

Liquid-liquid equilibrium measurements can be performed using a range of techniques with different types of equipment. Experimental methods for the measurement of liquid-liquid equilibria include the analytical method and the synthetic method (Weir and de Loos, 2005). For both methods, glass cells or jacketed glass cells are commonly used and the temperature of the samples in the cells are maintained by submersion of the cell into a thermostated bath or by means of a cooling or heating fluid that flows through the jacket.

3.2.1. Synthetic methods

The synthetic method is an optical method or a visual technique in which LLE is observed through the disappearance or appearance of turbidity due to immiscible phases appearing in the mixture (Matous et al., 2005). Using the synthetic method, the immiscible phases in the mixture cause an appearance or disappearance of murkiness or clouding which indicates liquid-liquid equilibrium. It is an optical method and is usually reported as cloud-point or clear-point data (Weir and de Loos, 2005). Glass jacketed cells are usually used for ease of observation. A thermal fluid flows through the jacket to control the temperature or the sealed vessel is submerged in the thermostated bath.

The turbidity of the mixture changes by metered changes in composition or by altering the temperature (Weir and de Loos, 2005). In the first method, a pseudo-titration is performed by slowly adding one of the components to the mixture (Weir and de Loos, 2005). This is done at a fixed temperature which results in a change in composition of the mixture until turbidity is observed. With the knowledge of the amounts of the components required for phase separation, the binodal curve can be constructed. For a more detailed discussion on the titration method, the reader can refer to the work of Briggs and Comings (1943), Rifai and Durandet (1962), Letcher et al. (1989) and Yang et al. (2021).

In the second method which is more commonly used, the composition is kept constant while the temperature is changed (e.g. Costa et al. (2012), dos Santos Gomes et al. (2019), Domańska and Marciniak (2005)). This is repeated until turbidity occurs. Note that accurate equilibrium tie lines cannot be measured experimentally using this method.

3.2.2. Analytical methods

In the analytical method, a synthetic mixture of known overall composition is prepared, placed in the measurement vessel in a thermostated environment and allowed to reach liquid-liquid phase equilibrium at the desired temperature and usually atmospheric pressure. The compositions of the two immiscible phases are determined by analysis. After the mixture is fed into the glass vessel, it undergoes rigorous stirring and is thereafter left to settle until it reaches equilibrium. At equilibrium, a distinct phase boundary forms and two separate liquid phases are observed. Samples may be drawn from the apparatus by the use of a syringe (Raal and Mühlbauer, 1998), or in other equipment pipettes have been used (Weir and de Loos, 2005).

The compositions in each liquid phase are thereafter determined. There are many techniques used to determine the composition of each phase. Some examples of such techniques are refractive index, identification by chemical reaction or titration, boiling point/ thermal conductivity differences (gas chromatography), solubility in solvents (liquid chromatography), density and others (Weir and de Loos, 2005). Gas or liquid chromatography is the preferred analysis method (Moriyoshi et al., 1989). The direct analytical method has the advantage of obtaining the binodal curve and the tie-line data simultaneously, since joining all tie-line data forms the binodal curve. This is an advantage over the synthetic method. This method is also applicable to systems containing more than three components (Novák et al., 1987).

Figure 3.3.a shows a classical thermostated vessel in which samples are taken from the individual phases from above using an injection syringe or from below using an outlet stopcock. The outlet stopcock is not usually well thermostated and has dead space. This approach is not ideal as these flaws contribute to errors to equilibrium and composition measurement. To prevent contamination of the equilibrium phases when sampling, the classical equilibrium cell was modified to prevent mutual contamination of the equilibrium phases during taking of samples from the bottom phase, hence it is not necessary to pass through the upper phase when taking samples from the lower phase (Rehak, 1999). The modified cell shown in Figure 3.3.b consists of a thermostated jacket, in which the cell with a magnetic stirrer is placed, and a side tube which is fitted to the bottom of the vessel with an injection syringe.

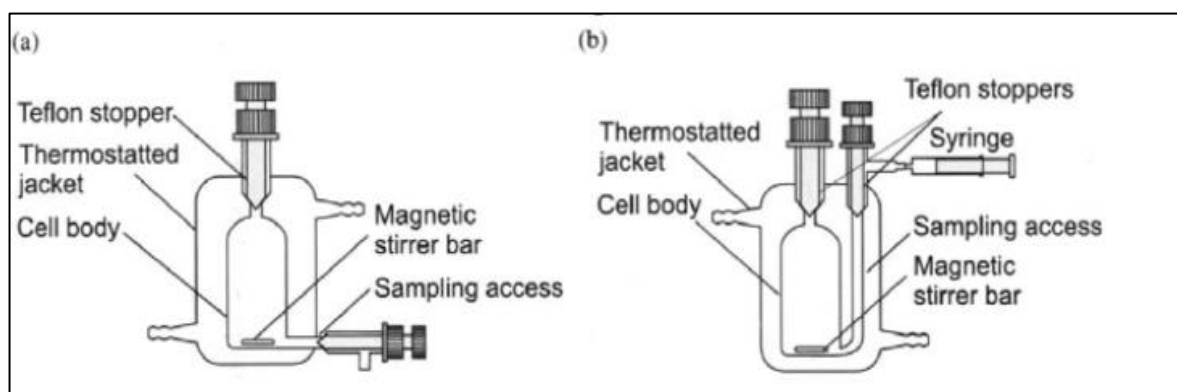


Figure 3.3. Thermostatted cells for determining liquid-liquid equilibria (a) classical form (Rehak, 1999) , (b) improved form with a side arm (Novák et al., 1987).

Figure 3.4 shows a two-position cell used by Lohmann et al. (1998). This equilibrium cell is thermostated with a cryostat liquid flowing through the jacket. The cell is automatically shaken to support the mass transfer between the phases (Figure 3.4.a). The two phases are continuously mixed for at least 12 hours. Figure 3.4.b shows the cell being turned over for the separation of the two phases A and B. Samples are taken from the two phases once they have been separated.

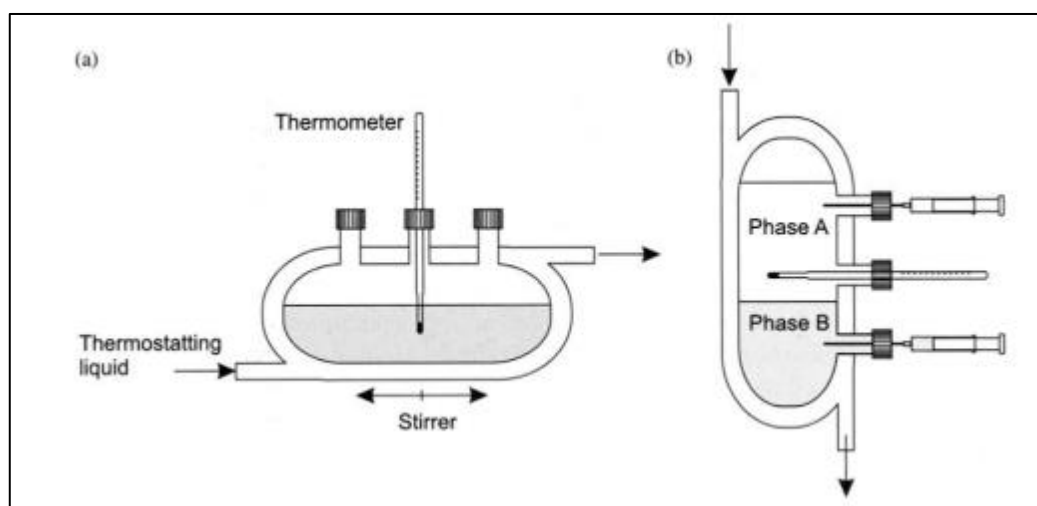


Figure 3.4. A two-position thermostated cell for measuring of liquid-liquid equilibria, (Lohmann et al., 1998).

Figure 3.5 shows an LLE apparatus used by Katayama and Ichikawa (1995) in which the LLE apparatus was assembled in an adiabatic stainless-steel bath. The apparatus consisted of a temperature regulator unit, cooler unit, three agitators for stirring the liquid in the bath, and three magnetic stirrer pads in which 100cm³ flasks were mounted on. The ternary mixture was poured into the flask and immersed in the bath. The mixtures were stirred for 3 hours and left to stand for 12 hours for equilibrium to be reached. Liquid samples are withdrawn separately for the two phases using a glass syringe.

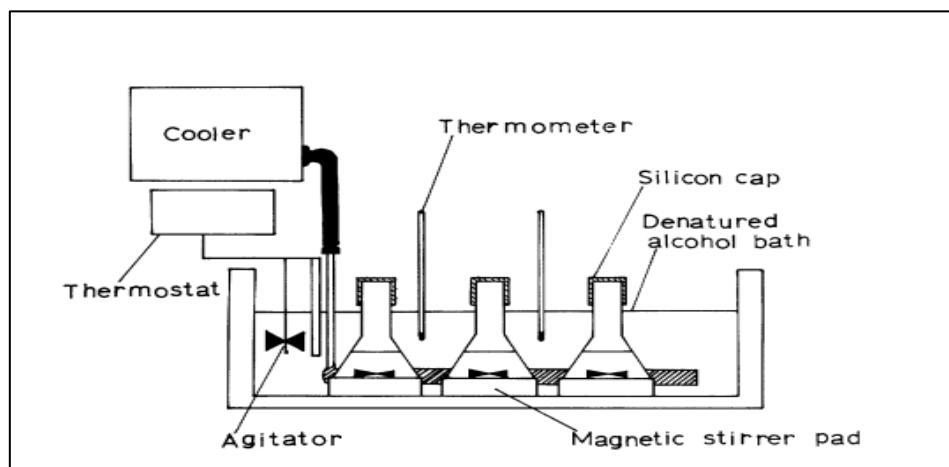


Figure 3.5. LLE apparatus in adiabatic stainless steel bath (Katayama and Ichikawa, 1995).

3.2.3. Liquid-Liquid Equilibrium Apparatus of Ndlovu (2005)

In this work, the direct analytical method was employed to obtain LLE data by use of a double-walled glass cell, and gas chromatography to determine the equilibrium phase compositions. The cell used in this work was a replica of a modification of the one used by Raal and Brouckaert (1992) and commissioned by Ndlovu (2005). The details of this equipment used and equilibration procedure follows.

3.2.3.1. Cell description.

The modified doubled-walled glass cell of Ndlovu (2005)(Raal and Brouckaert, 1992) was used in this work for the liquid-liquid equilibrium measurements. Figure 3.6 shows the 50 cm³ cell that was used with the experimental layout shown in Figure 3.7. This cell was successfully used in the studies of Narasigadu et al. (2009), Lasich et al. (2011) and Narasigadu et al. (2014). Being double walled, the temperature of the cell was controlled by flow of a thermostated fluid through the jacket from an oil bath. The cell lid contains a thermal well in which a temperature sensor is placed. The cell contained two sampling points for each liquid phase which allow for a higher accuracy during sampling for composition analysis. Samples for analysis were drawn from the top and bottom sampling points of the cell without disturbing the adjacent phase. A

magnetic stirrer bar was placed inside the equilibrium cell, and the filled cell was placed on a stirrer plate to induce mixing.

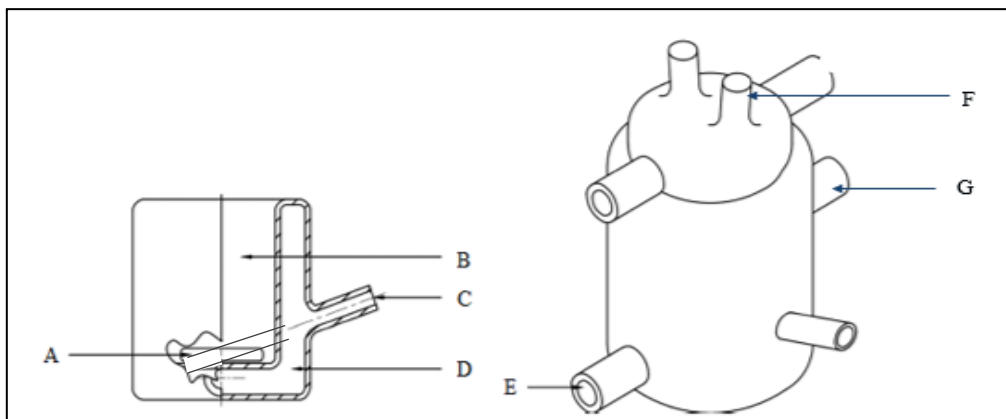


Figure 3.6. Schematic of modified doubled-walled glass cell of Ndlovu (2005) used in this work as shown in Narasigadu et al. (2014).

In Figure 3.6 (A) 14 mm stirrer bead; (B) Inner cell cavity; (C) Bottom sample point; (D) Cell wall cavity for heating fluid; (E) Cell heating fluid inlet; (F) Top sample point; (G) Cell heating fluid outlet

3.2.3.2.LLE apparatus components

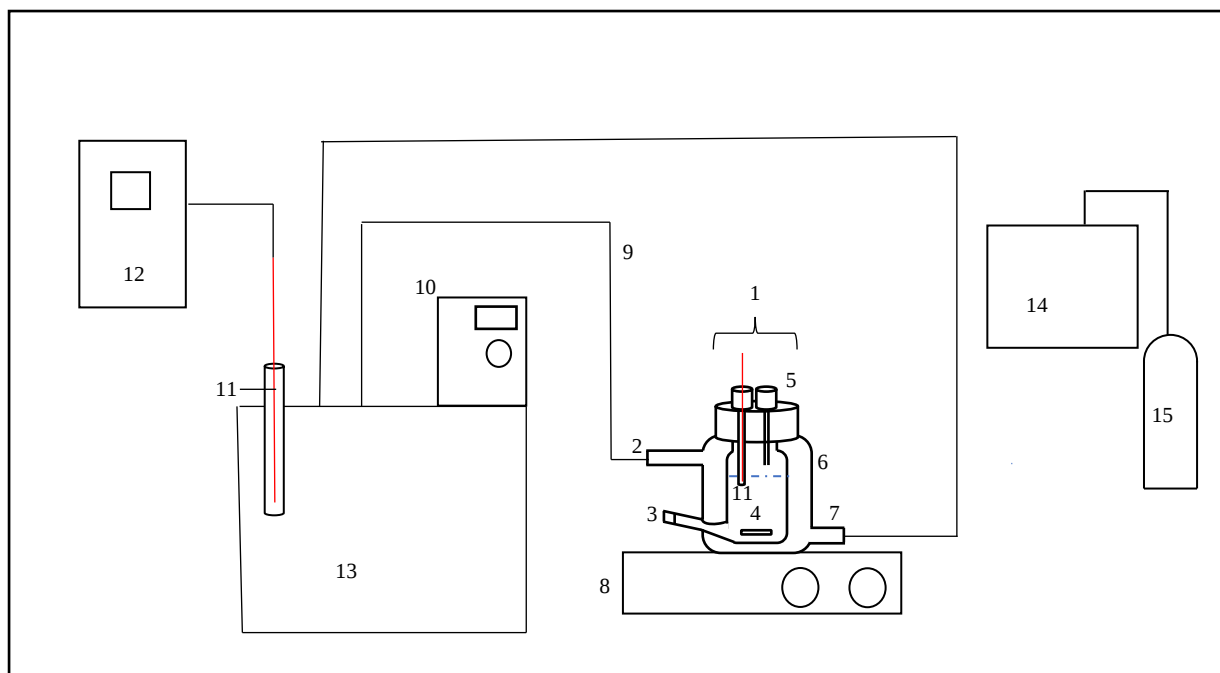


Figure 3.7. Layout of the apparatus of Ndlovu (2005) used in this work.

1-LLE double walled glass cell. 2-Oil inlet. 3-Bottom sample point. 4-Magnetic stirrer bar. 5- Top sample point. 6- Jacket. 7- Oil outlet. 8- Stirrer plate. 9- Oil pipe. 10- Circulator. 11 - Pt100 sensor, 12 -Digital Temperature Display, 13- Oil bath with temperature controller and pump, 14-SHIMADZU Gas Chromatograph, 15- Helium carrier gas

3.2.4. Calibrations and equilibration procedure

3.2.4.1.Temperature measurement

A Pt-100 class-A temperature sensor was used to measure the equilibrium temperature. An oil bath equipped with a circulating pump (Grant TX150) was used to maintain the jacketed vessel at a constant temperature. The temperature sensor used to measure the equilibrium temperature was alternated between the cell thermowell as well as in an oil test tube placed inside the thermostated oil bath, to ensure they correlated. The standard combined uncertainty of the temperature measurement was calculated to be 0.1 K from calibration using the WIKA CTB 9100 temperature standard.

3.2.4.2.Composition measurement

Phase composition analysis was conducted by gas chromatography analogously to the VLE measurement procedure. TCD calibration was required for the immiscible pair of LLE components in addition to the binary calibrations conducted for the miscible pairs in the VLE measurements. The internal standard procedure was used to create soluble mixtures for calibration with acetone used as the solvent. The standard combined uncertainty in composition for the ternary measurements was determined to be 0.005 mole fraction from calibration.

3.2.4.3.Equilibration procedure

The atmospheric pressure at equilibrium was measured using a CPC 6000 WIKA standard, and a standard uncertainty of 1 kPa was calculated. All the LLE data were measured at constant temperatures. A synthetic mixture of 2 or 3 components was prepared and placed in the vessel. It was ensured that the system formed two phases. The temperature of the oil bath was set, and the fluid was circulated. The mixture inside the vessel was stirred using a stirrer bar with a magnetic stirrer plate. The stirring speed was adjusted by trial and error to ensure a vortex was formed. A timer plug was used to allow the system to stir for 8 hours, and then settle for 12 hours. These times were established by trial and error, when sampling showed that no further changes in composition were observable after longer intervals. After stirring and settling the phases were analysed carefully with 3-5 parallel samples. After completion of the measurements, the magnetic stirrer and temperature controller were switched off and the still was allowed to cool before being cleaned.

CHAPTER FOUR

Isothermal vapor-liquid equilibrium (P-x-y) measurements and modeling of n-hexane + pentan-2-one/4-methylpentan-2-one

Chetty, T., Naidoo, P. and Moodley, K., 2020. Isothermal Vapor–Liquid Equilibrium (P–x–y) Measurements and Modeling of n-Hexane+ Pentan-2-one/4-Methylpentan-2-one. *Journal of Chemical & Engineering Data*, 65(11), pp.5567-5580.

4.1. Abstract

Isothermal vapour-liquid equilibrium (VLE) data were measured for the hexane + pentan-2-one/4-methylpentan-2-one systems to characterize the separation limits. Phase equilibrium measurements were undertaken at approximately 313, 323 and 334 K at sub-atmospheric pressures using a dynamic apparatus. The γ - Φ regression approach was used with the non-random two-liquid or UNIQUAC activity coefficient models employed to account for the non-ideality of the liquid phase, with the Hayden and O'Connell correlation in the virial equation of state, used to account for the vapour phase non-ideality. Additionally, the data were modelled by the ϕ - ϕ approach with the Peng-Robinson and Perturbed-Chain Statistical Associating Fluid Theory equations of state, which exhibited an inferior performance in comparison to the modelling by γ - Φ approach. The Area and Point thermodynamic consistency tests were applied to the data and showed that the measured data were thermodynamically consistent. Excess enthalpy predictions were found to correlate well with available literature.

4.2. Introduction

Oxygenated hydrocarbons including alcohols, aldehydes and ketones are found in the product and waste streams of the Fischer-Tropsch process (De Klerk, 2008). In the Fischer-Tropsch process carbon monoxide and hydrogen are converted into liquid hydrocarbons, while these oxygenates are formed from side reactions. Separation of these mixtures into pure components is vital as they are used in various applications in the petrochemical and solvent industries (Alvarez et al., 2007; Lv et al., 2016; Vázquez-Ojeda et al., 2013) and as feedstock in product development. Therefore, knowledge of the separation and blending limits of these mixtures is important. Process design for these separation processes rely heavily on experimental data as predictive methods for these complex systems require model binary interaction parameters that are not readily available in literature and are often proprietary knowledge.

Due to regulations imposed on leaded fuel in the last decade, increasing attention has been given to the further improvement of low octane number (ON) transport fuels (Çakmak et al., 2020; Christensen et al., 2011; Demirbas et al., 2015; Goh et al., 2012; Naqvi et al., 2018; Oparina et al., 2020; Rankovic et al., 2015; Rodríguez-Fernández et al., 2020). High octane quality of unleaded gasoline can be obtained more easily by the addition of oxygen containing fuel components. Alcohols and ketones can be used as oxygenated additives in unleaded gasoline to improve octane number (Agarwal, 2007). An important consideration for the use of oxygenated compounds in the fuel industry is the separation and blending potential of these fuels with alkanes and alkenes (the main components of petrol and diesel), as this affects their capacity to absorb water by hydrogen bonding from the atmosphere, or when live steam is used in refining (Araki et al., 2011; Bonner and Choi, 1974; Groysman, 2014). Water content in transport fuels must of course be limited.

Vapour-liquid equilibrium (VLE) data is necessary to characterize the blending of normal hydrocarbon and oxygenated hydrocarbon mixtures with different thermophysical behaviours for process design. This information is limited in the literature, especially for C6-C9 alkanes with C5 and C6 ketones (Arnold et al., 1987, 1982; Castells et al., 2000; Lecat, 1946; Pecsar and Martin, 1966; Scheller and Rao, 1973; Takeo et al., 1979; Wisniak, 1999), with little data available for the reported mixture combinations in this study (one isobaric study at 100 kPa by Marrufo et al.

(2011)). For this reason, VLE data measurements and data regression were performed for the binary mixtures of n-hexane (1) + pentan-2-one (2)/ 4-methylpentan-2-one (2) at approximately $T = 313.3, 323.3, \text{ and } 333.5 \text{ K}$. These temperatures were selected to maintain the n-hexane within its normal boiling point and, for practical and economic purposes such as maintaining process design limits within atmospheric pressure, and so that normal cooling water utilities can be suitably employed in the potential separation process with an approach of 12-20 K (Luyben, 2012, 2004; Xia et al., 2020). The experimental data were modelled using the combined γ - Φ method, with the non-random two-liquid (NRTL) (Renon and Prausnitz, 1968) and Universal Quasi-Chemical (UNIQUAC) (Abrams and Prausnitz, 1975) activity coefficient models, and with the Hayden and O'Connell (1975) correlation for the virial equation of state parameters. The thermodynamic consistency area test of Redlich and Kister (1948) and the point test of Christiansen and Fredenslund (1975) were conducted to assess the consistency of the experimental data.

4.3.Theory

The γ - Φ approach employs an activity coefficient model to determine the liquid phase non-idealities and an equation of state to determine the fugacity coefficient which accounts for the non-idealities in the vapour phase.

The γ - Φ formulation for VLE at low and moderate pressures is represented as follows:

$$y_i \Phi_i P = x_i \gamma_i P_i^{sat} \quad (4.1)$$

Where x_i and y_i are the liquid and vapour compositions of component i , P is the system pressure, P_i^{sat} is that saturation pressure of component i , and γ_i is the activity coefficient of component i .

Φ_i is a correction factor which is expressed by:

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \exp \left[\frac{-V_i(P - P_i^{sat})}{RT} \right] \quad (4.2)$$

Where $\hat{\phi}_i$ is the fugacity coefficient in solution, ϕ_i^{sat} is the saturation fugacity coefficient, V_i is the saturated liquid molar volume, R is the Universal gas constant, and T is the system temperature. $\hat{\phi}_i$ and $\hat{\phi}_i^{sat}$ can be determined by an equation of state. For sub-atmospheric pressures, the virial equation of state is suitable (Raal and Mühlbauer, 1998; Walas, 2013), where for a binary system equation 4.2 can be expressed by:

$$\Phi_i = \exp \left[\frac{(B_{ii} - V_i)(P - P_i^{sat}) + P y_j^2 \delta_{ij}}{RT} \right] \quad (4.3)$$

Where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (4.4)$$

The Hayden and O'Connell (1975) correlations were used to estimate the second virial coefficient (B_{ij}) values. The method is simple and applicable to various compounds of polar and associating systems (Walas, 2013). The activity coefficients of the compounds in the liquid phase were determined using the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models as they are suitable for the component combinations considered in this work (Walas, 2013).

The Gibbs excess energy is given by the summability relation:

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i \quad (4.5)$$

The change of the Gibbs Excess energy, G^E , with temperature is given by the Gibbs-Helmholtz relation and can be used to define the excess enthalpy, H^E ,:

$$H^E = -RT^2 \left[\frac{\partial \left(\frac{G^E}{RT} \right)}{\partial T} \right]_{P, x_i} \quad (4.6)$$

In the ϕ - ϕ approach to VLE modelling, a single equation of state is used to account for the non-idealities in both the liquid and vapour phases via the isofugacity condition of the fugacities in solution. Two equations of state were used in this work to model the data by the ϕ - ϕ approach, i.e. the Peng-Robinson equation of state (Peng and Robinson, 1976) (PR) and the Perturbed-Chain Statistical Associating Fluid Theory (Gross and Sadowski, 2001) (PC-SAFT) equation of state. The PR equation of state is based on the Van der Waals (1910) equation of state and the modifications of Redlich and Kwong (1949), and is stated to have improved mixing rules and performance near the critical region. The PC-SAFT model is based on the SAFT theory with a modification to use hard-chains as the reference fluid. It is stated to provide superior representation of polar components. Details of these models and their extensive formulation can be found in the original publications.

4.4.Experimental

4.4.1. Materials

All chemicals used were sourced from Sigma-Aldrich with the supplier stated mass purities exceeding 0.99 mass fraction. A Shimadzu GC 2014 gas chromatograph (GC) equipped with a thermal conductivity detector was used to confirm the purities by analysis of the pure samples. The GC analysis for the pure components resulted in relative GC peak areas of >0.99 fraction. Karl-Fischer titration, density and refractive index measurements were also conducted. Densities were measured at $T = 298.15$ K using an Anton Paar DSA 5000M apparatus with a supplier stated accuracy of $0.007 \text{ kg}\cdot\text{m}^{-3}$. Refractive indices of the pure chemicals were determined at $T = 293.15$ K by using an ATAGO RX-7000 α refractometer (sodium D-line = 589 nm) with a supplier uncertainty of 0.0001. Karl Fischer titrations were performed using an MKS 500 device to determine the water content of the ketones. The water content of the ketones used were found to be below 0.0005 mass fraction. The details of the chemical purities and suppliers are provided in Table 4.1.

4.4.2. Equipment and uncertainties

For VLE measurements, the dynamic apparatus originally reported by Joseph et al. (2001) was used with minor modifications to auxiliary parts such as the pressure transducer (WIKA P-10) and

measurement displays (Shinko ACS and ABB series). A schematic of the apparatus is shown in Figure 4.1. The operating procedure described by Joseph et al. (2001) was used, with the exception of temperature being controlled manually in this work by observing the plateau region of constant temperature over heating rate and drip rate at equilibrium. The system was deemed to be at equilibrium when the temperature and pressure in the plateau region was constant for 1 hour, and a condensation drip rate of 1 drop per second was observed. Vapour pressure measurements were conducted three times at the same temperature and averaged. An ABB F080 pressure controller was used to maintain pressure which subjected the VLE apparatus to vacuum or vented the unit to the atmosphere to maintain the desired setpoint pressure. Equilibrium sampling for each phase was conducted using a gas-tight GC syringe in triplicate with relative differences less than 0.01 between parallel sample compositions. Equilibrium temperatures and pressures were also noted in triplicate (at each sampling time). A POROPAK-Q column (2 m x 2.2 mm) was used, with helium as the carrier gas for GC analysis. A temperature of 513.15 K for the injector, column and detector and a flow rate of 30 ml/min for the carrier gas was found to be the optimum GC conditions. The same GC and conditions were used for the pure component analysis above.

A WIKA P-10 transducer (0-100 kPa) was used to measure the equilibrium pressure. This transducer was calibrated using a WIKA CPC 3000 pressure controller as a standard with an uncertainty of 0.02 kPa. The supplier uncertainty for the WIKA P-10 transducer was stated as 0.05 kPa and the standard combined uncertainty in pressure was calculated to be 0.1 kPa. Temperature was controlled by a voltage supply to a heater cartridge within a glass sleeve in the boiling chamber and insulation was used to reduce heat losses. A class-A Pt-100 temperature probe was used to measure the equilibrium temperature within the equilibrium chamber. This probe was calibrated using a WIKA CTB 9100 temperature standard with reported uncertainty of 0.05 K. The standard combined uncertainty in temperature was calculated to be 0.1 K. The thermal conductivity detector of the gas chromatograph was calibrated by using the area ratio method of Raal and Mühlbauer (1998). The standard mixtures for the calibration were prepared gravimetrically. A Mettler-Toledo mass balance (model AB204-S) with a readability of 0.0001g was used. This device is calibrated with standard weights. The standard combined uncertainty in composition was calculated to be 0.005 mole fraction. For all uncertainty calculations, procedures outlined by NIST JCGM(ISO, 2008) were followed. The combined uncertainties were calculated by type A and type B

propagation of errors and took into account the supplier uncertainty, uncertainty from calibration, uncertainty from repeatability and the uncertainty introduced by chemical impurity in the relevant calculations. Table 4.2 lists the uncertainties associated with the reported variables studied in this work.

4.5. Results and Discussion

The experimentally measured pure component vapour pressures were compared to calculated values from the Antoine prediction using the parameters reported by Poling et al. (2001) and the Wagner equation using parameters available in NIST TDE (NIST, 2019). These results are shown in Table 4.3. There is a close correlation between the experimental and calculated data. The RMSD (defined below) was calculated to be 0.1 kPa with a maximum deviation of 0.3 kPa for n-hexane at 323.3 K. The differences can be attributed to the combined effect of the uncertainties in experimental temperature and pressure measurements, as well as the small amount of impurity in the pure components and are within the propagated error of the reported uncertainties in these variables.

The experimental VLE data for the n-hexane (1) + pentan-2-one (2) system at 313.3, 323.3 and 333.5 K and the hexane (1) + 4-methylpentan-2-one (2) at 313.3, 323.3 and 333.6 K are presented in Tables 4.4 and 4.5 and graphically in Figures 4.2 and 4.3, respectively. Comparison to previously measured data was not possible for the n-hexane (1) + pentan-2-one (2) system as no VLE data has been reported in the literature for this system. The system exhibits strong positive deviation from Raoult's law. Azeotropic behaviour was observed for the n-hexane (1) + pentan-2-one (2) system at all measured temperatures. Similar behaviour has been observed for other alkane-ketone systems such as the n-hexane (1) + butan-2-one system (Maripuri and Ratcliff, 2007) and the n-hexane (1) + pentan-3-one (2) system (Barraza et al., 1979). Isobaric data has been measured for the hexane (1) + 4-methylpentan-2-one (2) system at 100 kPa by Marrufo et al. (2011). Since the conditions do not overlap with those measured in this work, it is not possible to make direct comparisons, or reasonable quantitative extrapolations. Nevertheless, in Figure 4.3, the P-x-y data point at approximately 343 K from the study is presented. It can be seen that with increasing temperature in 10 K intervals, that the general trend in the P-x-y behaviour is reasonably maintained.

The VLE data was correlated using the γ - Φ approach with the NRTL and UNIQUAC models, and the virial equation of state with the Hayden and O'Connell correlation. Therefore, the model combinations were NRTL-HOC and UNIQUAC-HOC. The Hayden and O'Connell correlation parameters are calculated automatically for each system using in-built pure component parameters in the ASPEN Plus ® V.10 database. For each system, model parameters were determined for each activity coefficient model simultaneously for the three isotherms using ASPEN Plus ® V.10 software by minimizing the following expression for the Root Mean Square Deviation (RMSD) using the Britt-Luecke algorithm:

$$RMSD = \sqrt{\frac{\sum_{k=1}^N (P^{exp} - P^{calc})^2}{N}} \quad (4.7)$$

Where N is the number of data points measured and P^{exp} and P^{calc} are the measured and model-calculated pressures respectively. This objective function has been recommended by Van Ness and Abbott (1982).

The absolute average deviation (δy_1) in vapour composition was calculated using the following expression:

$$\delta y_1 = \frac{abs(y_1^{exp} - y_1^{calc})}{N} \quad (4.8)$$

In Figures 4.2 and 4.3 the model calculated VLE results are presented for the systems of n-hexane (1) + pentan-2-one (2) and n-hexane (1) + 4-methylpentan-2-one (2) at the three temperatures. The RMSD values and model parameters are shown in Table 4.6. A good correlation between the calculated and experimental pressure data is observed as the RMSD values do not exceed 0.048 kPa, which is within the experimental uncertainty in pressure. While the NRTL-HOC and UNIQUAC-HOC model correlations are very similar with RMSDs in pressure and Absolute Average Deviations (AAD) in vapour composition differing only by the third decimal, by observation of the model deviations, the UNIQUAC-HOC model performs slightly better than the NRTL-HOC model.

The thermodynamic consistency tests were performed on the experimental VLE data by using the area test of Redlich and Kister (1948) and the point test of Christiansen and Fredenslund (1975) by fitting to a Legendre polynomial. This was done using ASPEN Plus ® V10 software with the default criteria of 10% tolerance for the area test and 0.01 deviation for the point test as recommended by the authors of the tests. The results confirm that the data is thermodynamically consistent according to these tests and are presented in Table 4.7. The data was also found to pass the infinite dilution test of Kojima et al. (1990) using the standard tolerances.

The n-hexane (1) + pentan-2-one (2) system displays azeotropic behaviour at all measured temperatures. These are presented in Table 4.8. The n-hexane composition of the azeotrope increases with increasing temperature. For the n-hexane (1) + 4-methylpentan-2-one (2) system azeotropic behaviour was not observed experimentally.

In Figures 4.4 and 4.5, the activity coefficient behaviour for each system at 313.3 K is shown. For both systems, the activity coefficients are well represented by the models, with slight asymmetry of the activity coefficient plots being related to the highly non-ideal behaviour of the systems. The infinite dilution activity coefficients predicted by each model are presented in Table 4.9. Extrapolation by the model independent method of Maher and Smith (1979) is also presented for comparison. A decrease of the infinite dilution activity coefficient with temperature was generally observed from the extrapolations. This information is useful for high-purity separation design.

The change in the experimental and model calculated relative volatilities ($\alpha_{ij} = \frac{y_i}{x_i} / \frac{y_j}{x_j}$) with composition are presented in Figures 4.6 to 4.9. The α_{12} trends were generally found to decrease with increasing temperature, with the opposite behaviour for α_{21} . This is an expected trend. It can be seen that there is a reasonable correlation between the experimental and model calculated relative volatilities, and a general smoothness, with a slight deviation in the n-hexane + pentan-2-one system at 313.3 and 333.5 K, and for the n-hexane + 4-methylpentan-2-one system at 323.3 K, which further confirms the precision of the composition measurements. Small deviations are attributed to the very high sensitivity of α_{12} to small differences between experimental and calculated composition values which is amplified near the pure component points (Gmehling et

al., 2019). A composition deviation within the experimental uncertainty can lead to changes in α_{ij} exceeding 5 to 15 % and exceeding 35% in the dilute regions.

The plots of $\frac{G^E}{RT}$ and $\frac{H^E}{RT}$ are presented in Figures 4.10 to 4.13 along with the UNIQUAC-HOC model prediction. A positive G^E is observed for both systems and there is a reasonable correlation between the experimental and UNIQUAC-HOC model (the best fit model) excess Gibbs energies for most systems and conditions. The prediction is however poor for the n-hexane (1) + 4-methylpentan-2-one (2) system at 333.6 K. This is attributed to the use of a single set of parameters to represent all three isotherms which is necessary for the prediction of the excess enthalpies by the model.

The $\frac{H^E}{RT}$ predicted using the regressed UNIQUAC-HOC model (the best fit model) was compared to the available literature (Kiyohara et al., 1977) for the n-hexane + pentan-2-one system in Figure 4.12. A very good correlation is observed which further validates the quality of the experimental VLE data and the model fit. In Figure 4.13 the $\frac{H^E}{RT}$ plot for the n-hexane + 4-methylpentan-2-one system is presented. It can be seen that the excess enthalpy is also positive but slightly more asymmetrical, with the maxima occurring at approximately 0.64 mole fraction n-hexane, compared to the maxima of ~ 0.6 for the n-hexane + pentan-2-one system. The difference may be attributed to the different molecule sizes of the two ketones as well as the resultant differences in the intermolecular interactions typical of alkane + ketone mixtures.

The data were also modelled by the ϕ - ϕ approach by employing the PR and PC-SAFT equations of state and again minimizing the pressure residual as with the γ - Φ approach described above. The pure component parameters used for this modelling are provided at the end of this section in Table 4.10. A single binary interaction parameter (k_{ij}) for the mixing rule of each model and system was regressed. These results are presented in Table 4.6 along with the RMSDs in pressure and Absolute Average Deviations (AAD) in vapour composition. It can be seen that the activity coefficient models with the virial equation of state provide a superior representation of the experimental data. There is no significant difference between the performances of the PR and PC-SAFT models. This

is shown graphically in Figures 4.14-4.19, where comparisons to experimental P-x-y data and relative volatilities are shown.

4.6. Conclusion

Vapour-liquid equilibrium data for the ketone-alkane systems of n-hexane + pentan-2-one/4-methyl pentan-2-one were successfully measured using a dynamic apparatus which was operated at sub-atmospheric pressures. The measured data were found to be thermodynamically consistent which helped confirm the validity of the results obtained. The behaviour of the systems measured are highly non-ideal. The NRTL model with virial EOS (HOC) and UNIQUAC model with virial EOS (HOC) correlated the data well and outperformed the modelling by the ϕ - ϕ approach using the Peng Robinson and PC-SAFT equations of state. The values for the root mean square deviation (RMSD) in pressure were found to be within the experimental uncertainty. The RMSD values for VLE pressures were between 0.025 and 0.048 kPa. The Gibbs excess energy and excess enthalpy were found to be positive for the entire composition range, and the predicted excess enthalpy correlated well with literature where available.

Table 4.1. Details of chemicals used.

Component ^a	CAS RN.	Refractive index (RI) ^b		Density (kg.m ⁻³) ^d		Purity ^e (wt. fraction)	GC peak relative area
		Experimental	Literature ^c	Experimental	Literature		
n-hexane	110-54-3	1.3750	1.3750	655.02	654.9(Sastry and Valand, 1998) 655.3(Fang et al., 2008)	≥0.990	0.999
pentan-2-one	107-87-9	1.3899	1.3895	801.75	801.42(González et al., 2005) 801.91(Dománska et al., 2002)	≥0.995	0.999
4-methylpentan-2-one	108-10-1	1.3961	1.3962	795.98	795.94(Lladosa et al., 2011) 796.03(Marrufo et al., 2011)	≥0.990	0.999

^aAll chemicals purchased from Sigma Aldrich

^b RI measured at 293.15 K and 0.101 MPa. Standard uncertainties u are $u(RI) = 0.0001$, $u(T) = 0.05 K$, $u(P) = 0.1 kPa$,

^c Haynes(Haynes, 2014) at 293.15 K

^d Density measured at 298.15 K and 0.101 MPa. Standard uncertainties u are $u(\rho) = 0.2 \text{ kg.m}^{-3}$, $u(T) = 0.01 K$, $u(P) = 0.1 kPa$,

^eAs stated by the supplier

Table 4.2. Standard Uncertainty Estimates.

Source of uncertainty	Estimate	Distribution
Mass balance and impurity uncertainty (g)	0.0003 ^a	Rectangular
Repeatability of calibration (x_i)	0.001 ^b	Rectangular
Correlation of calibration (x_i)	0.001 ^a	Rectangular
Correlation for P (kPa absolute)	0.058 ^a	Rectangular
P measurement repeatability (kPa absolute)	0.058 ^b	Rectangular
P standard/kPa: Mensor CPC 3000 (100 kPa absolute)	0.020 ^a	Normal
Transducer standard uncertainty P /kPa (0.05 % of	0.029 ^a	Rectangular
Correlation for T (K)	0.058 ^a	Rectangular
T reference /K: CTH 6500	0.029 ^a	Rectangular
T measurement repeatability (K)	0.058 ^b	Rectangular

^a Estimate treated as a type A distribution.

^b Estimate treated as a type B distribution.

Table 4.3. Experimental vapour pressure data and comparison to Antoine and Wagner correlation.^a

Component	T/K		P/kPa	
		Experimental	Antoine correlation of Poling et al.(Poling et al., 2001)	Wagner equation of NIST TDE(NIST, 2019)
n-hexane	313.3	37.6	37.5	37.7
	323.3	54.8	54.5	54.6
	333.5	77.3	77.3	77.4
	333.6	77.8	77.6	77.8
pentan-2-one	313.3	10.0	10.0	9.98
	318.3	12.5	12.5	12.5
	323.3	15.7	15.6	15.6
	328.3	19.4	19.3	19.3
	333.5	23.8	23.8	23.8
	338.3	28.8	28.7	28.8
4-methylpentan-2-one	313.3	5.8	5.9	5.9
	323.3	9.4	9.4	9.4
	333.6	14.8	14.8	14.7

^a Standard combined uncertainties are $u(T) = 0.1 \text{ K}$, $u(P) = 0.1 \text{ kPa}$.

Table 4.4. Vapour-liquid equilibrium data for the n-hexane (1) + pentan-2-one (2) system. ^a

$T/K = 313.3$			$T/K = 323.3$			$T/K = 333.5$		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
10.0	0	0	15.7	0	0	23.8	0	0
11.2	0.012	0.115	17.0	0.009	0.090	25.5	0.009	0.074
12.4	0.026	0.214	17.9	0.018	0.141	27.4	0.019	0.147
13.3	0.037	0.275	18.3	0.020	0.162	33.7	0.062	0.330
13.5	0.040	0.284	19.1	0.025	0.201	34.1	0.068	0.339
17.2	0.086	0.464	21.5	0.046	0.303	41.7	0.123	0.489
19.2	0.115	0.530	23.7	0.065	0.378	46.0	0.155	0.549
21.3	0.151	0.591	24.9	0.076	0.413	50.1	0.202	0.602
25.0	0.213	0.676	27.6	0.103	0.482	53.8	0.248	0.639
27.0	0.264	0.712	29.0	0.122	0.515	54.8	0.259	0.649
29.4	0.356	0.745	32.5	0.161	0.580	56.5	0.283	0.667
30.4	0.385	0.766	34.5	0.188	0.612	58.3	0.313	0.689
32.2	0.498	0.791	37.1	0.236	0.650	60.3	0.360	0.709
34.9	0.638	0.840	39.1	0.278	0.681	62.5	0.402	0.725
35.9	0.719	0.859	40.7	0.313	0.703	65.5	0.479	0.754
36.8	0.839	0.890	43.1	0.372	0.734	66.9	0.515	0.769
36.9	0.840	0.892	44.1	0.391	0.744	72.0	0.663	0.822
37.7	0.986	0.985	47.1	0.497	0.786	73.8	0.721	0.843
37.6	1	1	51.8	0.721	0.849	74.8	0.772	0.859
			52.6	0.772	0.865	75.8	0.832	0.883
			53.0	0.809	0.884	76.5	0.875	0.899
			53.4	0.843	0.898	77.3	0.935	0.940
			54.0	0.892	0.922	77.5	0.982	0.980
			54.3	0.945	0.953	77.3	1	1
			54.5	0.977	0.980			
			54.4	1	1			

^a Standard combined uncertainties u are $u(T) = 0.1\text{ K}$, $u(P) = 0.1\text{ kPa}$, $u(x_i) =$, $u(y_i) = 0.005$

Table 4.5. Vapour-liquid equilibrium data for the n-hexane (1) + 4-methylpentan-2-one (2) system. ^a

T/K = 313.3			T/K = 323.3			T/K = 333.6		
P/kPa	x ₁	y ₁	P/kPa	x ₁	y ₁	P/kPa	x ₁	y ₁
5.8	0	0	9.4	0	0	14.8	0	0
6.1	0.002	0.042	10.2	0.006	0.084	15.2	0.003	0.033
6.2	0.003	0.058	10.7	0.010	0.129	15.4	0.004	0.046
6.5	0.006	0.104	11.4	0.016	0.187	15.9	0.008	0.079
6.9	0.011	0.159	13.5	0.034	0.324	17.1	0.016	0.146
7.3	0.015	0.208	15.0	0.049	0.400	17.6	0.020	0.175
8.8	0.035	0.353	16.6	0.065	0.466	20.8	0.046	0.320
14.2	0.123	0.623	20.1	0.102	0.573	23.0	0.062	0.395
15.5	0.145	0.661	21.4	0.118	0.604	26.9	0.094	0.498
17.4	0.182	0.708	22.1	0.130	0.621	33.1	0.149	0.615
19.0	0.221	0.743	23.1	0.141	0.642	35.0	0.166	0.641
20.6	0.259	0.770	24.1	0.155	0.660	38.6	0.202	0.687
22.7	0.306	0.801	24.4	0.159	0.666	46.7	0.290	0.764
24.8	0.364	0.828	27.5	0.208	0.716	47.7	0.304	0.773
24.9	0.365	0.829	31.9	0.273	0.767	49.7	0.332	0.790
25.2	0.389	0.834	33.9	0.314	0.789	53.2	0.383	0.815
25.8	0.400	0.841	36.9	0.363	0.818	56.2	0.437	0.837
25.9	0.402	0.842	37.4	0.375	0.822	56.5	0.446	0.840
26.4	0.418	0.848	39.0	0.412	0.836	59.3	0.488	0.854
27.0	0.438	0.854	41.9	0.499	0.863	60.1	0.513	0.861
27.4	0.453	0.858	44.4	0.564	0.882	62.9	0.581	0.879
28.2	0.488	0.866	46.9	0.637	0.900	64.9	0.627	0.890
31.3	0.626	0.899	48.1	0.676	0.910	65.8	0.653	0.896
32.4	0.693	0.910	49.3	0.739	0.920	69.3	0.743	0.915
33.4	0.743	0.921	50.7	0.820	0.934	71.8	0.808	0.929
34.5	0.807	0.934	51.9	0.859	0.946	72.6	0.837	0.936
35.3	0.848	0.943	52.7	0.890	0.954	72.8	0.855	0.939
35.7	0.869	0.949	53.7	0.949	0.972	74.2	0.891	0.949
35.8	0.878	0.952	54.5	0.990	0.991	75.2	0.920	0.958
36.9	0.948	0.976	54.8	1	1	76.3	0.951	0.972
37.5	0.991	0.995				77.6	0.990	0.991
37.6	1	1				77.8	1	1

^a Standard combined uncertainties u are $u(T) = 0.1\text{ K}$, $u(P) = 0.1\text{ kPa}$, $u(x_i) =$, $u(y_i) = 0.005$

Table 4.6. Regressed model parameters.^a

System	n-hexane (1) + pentan-2-one (2)	
Parameter		
	NRTL-HOC ^b	UNIQUAC-HOC ^c
a_{12}	-0.905	0.134
a_{21}	-0.512	0.0980
b_{12}/K	587	-205
b_{21}/K	326	8.19
$\alpha_{12, \text{NRTL}}$	0.533	-
RMSD/kPa	0.026	0.025
δy_1^*	0.006	0.005
	PR	PC-SAFT
k_{ij}	0.0588	0.0380
RMSD/kPa	0.099	0.087
δy_1^*	0.012	0.012
System	n-hexane (1) + 4-methylpentan-2-one (2)	
Parameter		
	NRTL-HOC ^a	UNIQUAC-HOC ^b
a_{12}	1.27	-0.553
a_{21}	0.541	0.227
b_{12}/K	-28.5	-4.89
b_{21}/K	2.42	-1.11
$\alpha_{12, \text{NRTL}}$	1.01	-
RMSD/kPa	0.048	0.047
δy_1^*	0.008	0.007
	PR	PC-SAFT
k_{ij}	0.0573	0.0333
RMSD/kPa	0.090	0.096
δy_1^*	0.010	0.011

^aModel parameters can be related to those described in the original works by the following expressions:

$$^b\tau_{ij, \text{NRTL}} = \left(a_{ij} + \frac{b_{ij}}{T}\right), G_{ij} = \exp(\alpha_{ij, \text{NRTL}}\tau_{ij, \text{NRTL}}),$$

$$^c\tau_{ij, \text{UNIQUAC}} = \exp\left(a_{ij} + \frac{b_{ij}}{T}\right)$$

$$^*\text{Absolute Average Deviation: } \delta y_1 = \frac{\text{abs}(y_1^{\text{exp}} - y_1^{\text{calc}})}{N}$$

Table 4.7. Results of thermodynamic consistency tests.

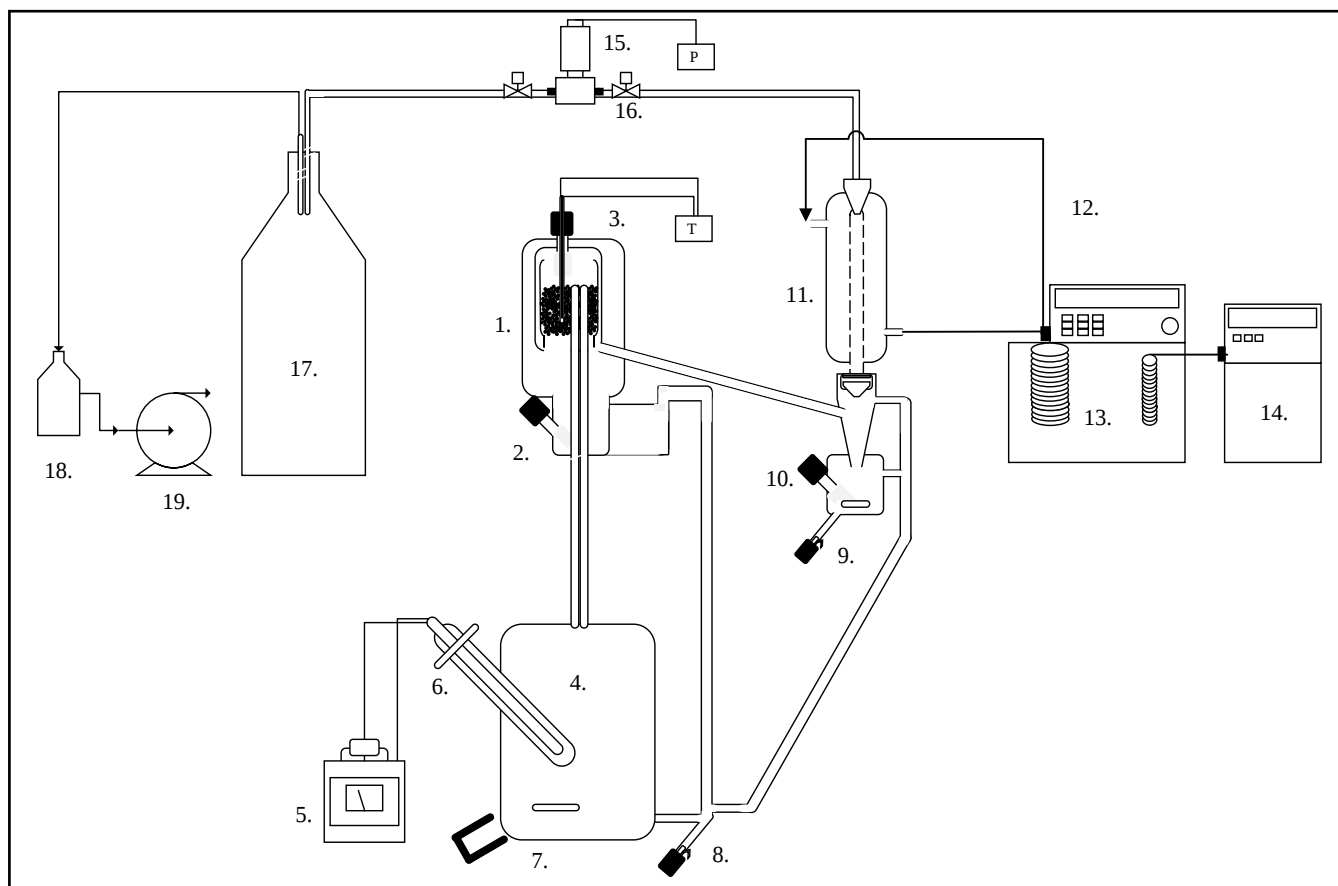
System	Calculated criterion		Consistency test result
	Area Test (%)	Point test	
n-hexane (1) + pentan-2-one (2)			
$T/K = 313.3$	0.135	0.004	Passed both tests
$T/K = 323.3$	3.854	0.004	Passed both tests
$T/K = 333.5$	2.381	0.004	Passed both tests
n-hexane (1) + 4-methylpentan-2-one (2)			
$T/K = 313.3$	3.749	0.005	Passed both tests
$T/K = 323.3$	3.830	0.002	Passed both tests
$T/K = 333.6$	5.051	0.005	Passed both tests

Table 4.8. Interpolated azeotropic conditions from experimental data and the UNIQUAC-HOC model.

System	Azeotrope conditions			
	Experimental		UNIQUAC-HOC	
	P/kPa	$x_1 = y_1$	P/kPa	$x_1 = y_1$
n-hexane (1) + pentan-2-one (2)				
$T / K = 313.3$	37.80	0.9492	37.80	0.9502
$T / K = 323.3$	54.55	0.9691	54.55	0.9603
$T / K = 333.5$	77.55	0.9703	77.55	0.9680

Table 4.9. Infinite dilution predicted by the NRTL-HOC and UNIQUAC-HOC models.

System	T/K	NRTL-HOC		UNIQUAC-HOC		Extrapolation (Maher and Smith, 1979)	
		γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
n-hexane (1) + pentan-2-one (2)	313.3	3.029	3.931	2.946	3.751	3.088	4.236
	323.3	2.882	3.644	2.820	3.512	3.050	3.289
	333.5	2.743	3.386	2.702	3.296	2.969	3.219
n-hexane (1) + 4-methylpentan-2-one (2)	313.3	2.478	4.439	2.249	3.515	3.030	3.555
	323.3	2.477	4.451	2.246	3.506	2.562	5.079
	333.6	2.476	4.463	2.243	3.498	2.442	5.091



**Figure 4.1. Schematic of the apparatus of Joseph et al. (2001) used in this work
extracted from Mavalal et al. (2019)**

1-Equilibrium chamber. 2-Liquid sampling port. 3-Temperature measurement. 4-Boiling chamber. 5- Variable heat supply to boiler. 6- Heater cartridge and sleeve. 7- Magnetic stirrer and bead. 8- Boiler drain valve. 9- Condensate drain valve. 10- Vapour condensate sampling point. 11- Condenser. 12- Coolant line to condenser. 13. Coolant bath and controller. 14- Chiller. 15- Pressure measurement. 16. Isolation valves. 17- Ballast tank. 18. Cold trap. 19. Vacuum pump.

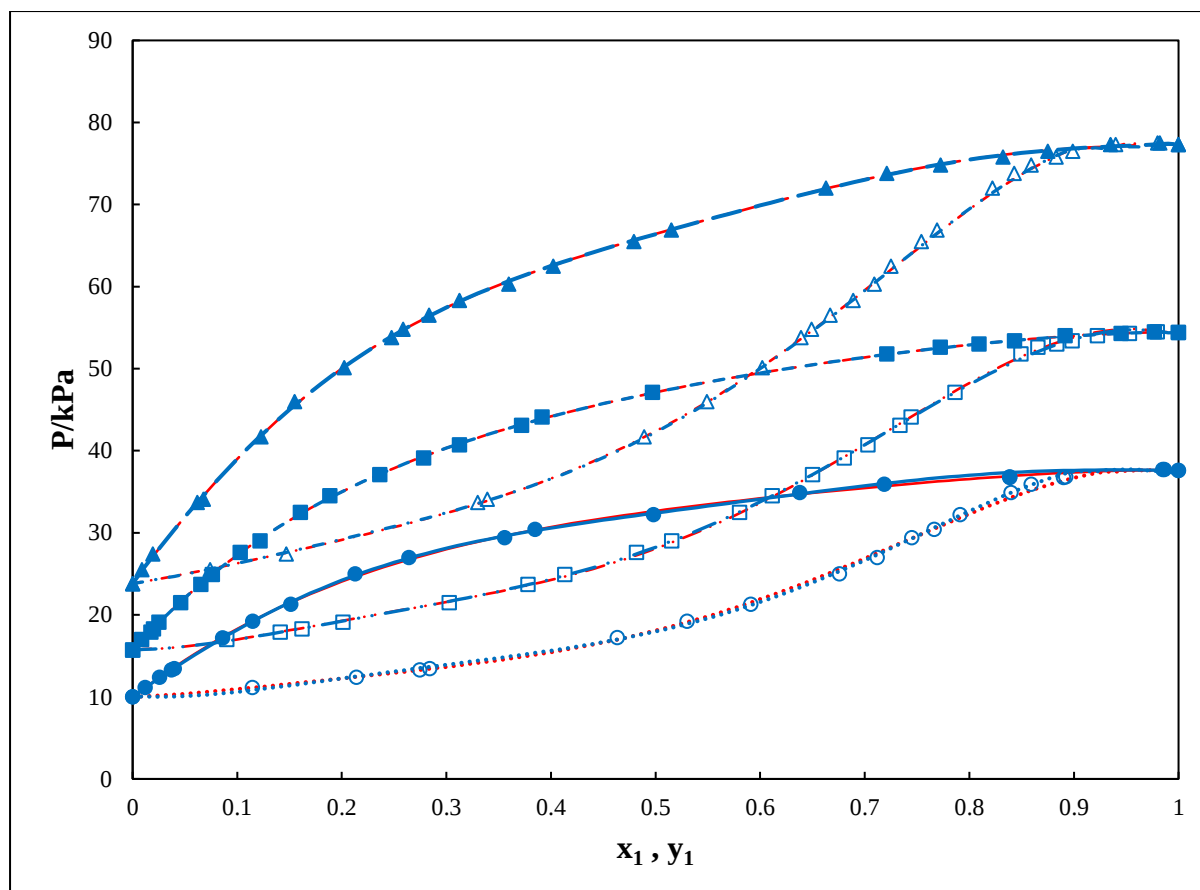


Figure 4.2. Vapour-liquid equilibrium data (P-x-y) for the n-hexane (1) + pentan-2-one (2) system at: (exp. x_1 , exp. y_1 , model x_1 , model y_1): 313.3 K, ($\bullet$, $\circ$, $-$, $\cdots$); 323.3 K, ($\blacksquare$, $\square$, $-$, $\cdots$); 333.5 K, ($\blacktriangle$, $\triangle$, $-$, $\cdots$). Red lines represent the NRTL-HOC model and blue lines represent the UNIQUAC-HOC model.

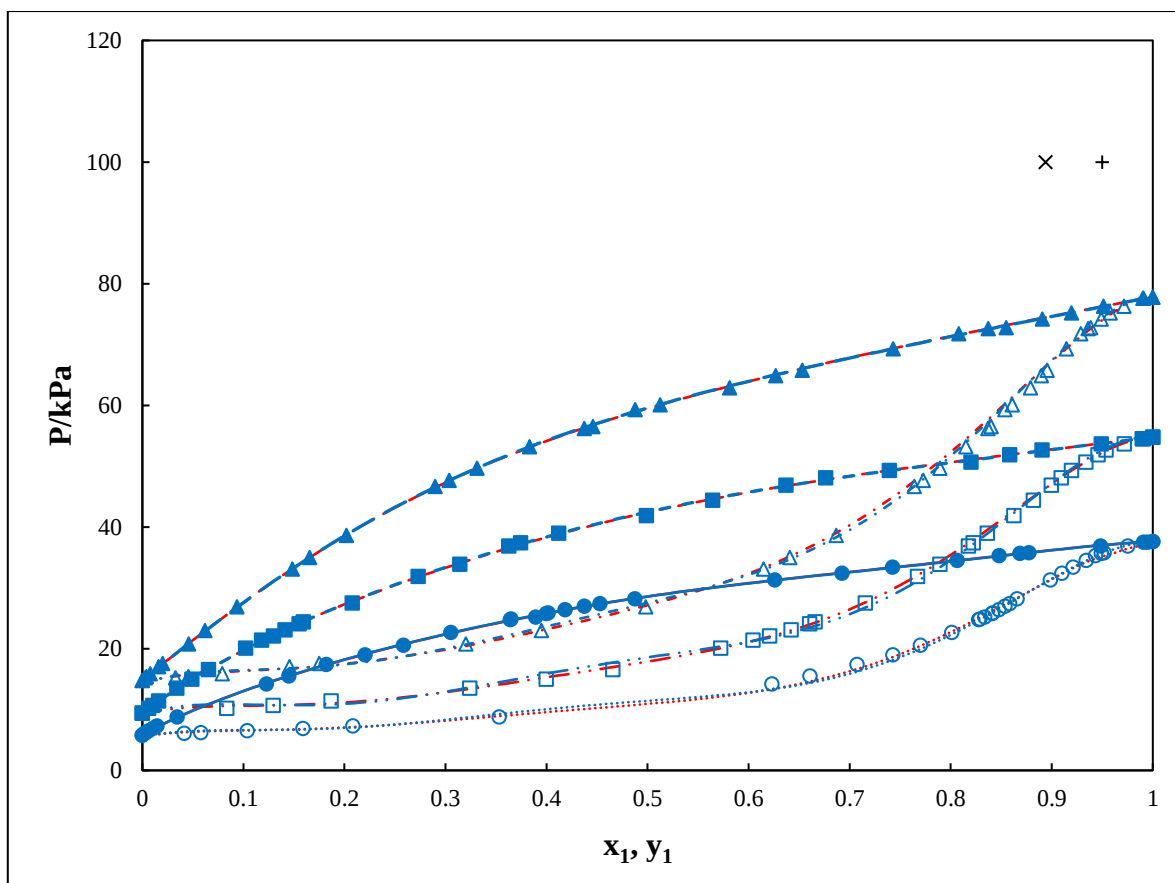


Figure 4.3. Vapour-liquid equilibrium data (P - x - y) for the n-hexane (1) + 4-methylpentan-2-one(2) system at: (exp. x_1 , exp. y_1 , model x_1 , model y_1): 313.3 K, ($\bullet$, $\circ$, $—$, $---$); 323.3 K, ($\blacksquare$, $\square$, $---$, $---$); 333.6 K, ($\blacktriangle$, $\triangle$, $---$, $---$). Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model. Literature data at 343.03 K and 100 kPa: (lit. x_1 , lit. y_1) ($\times$, $+$) (Marrufo et al., 2011).

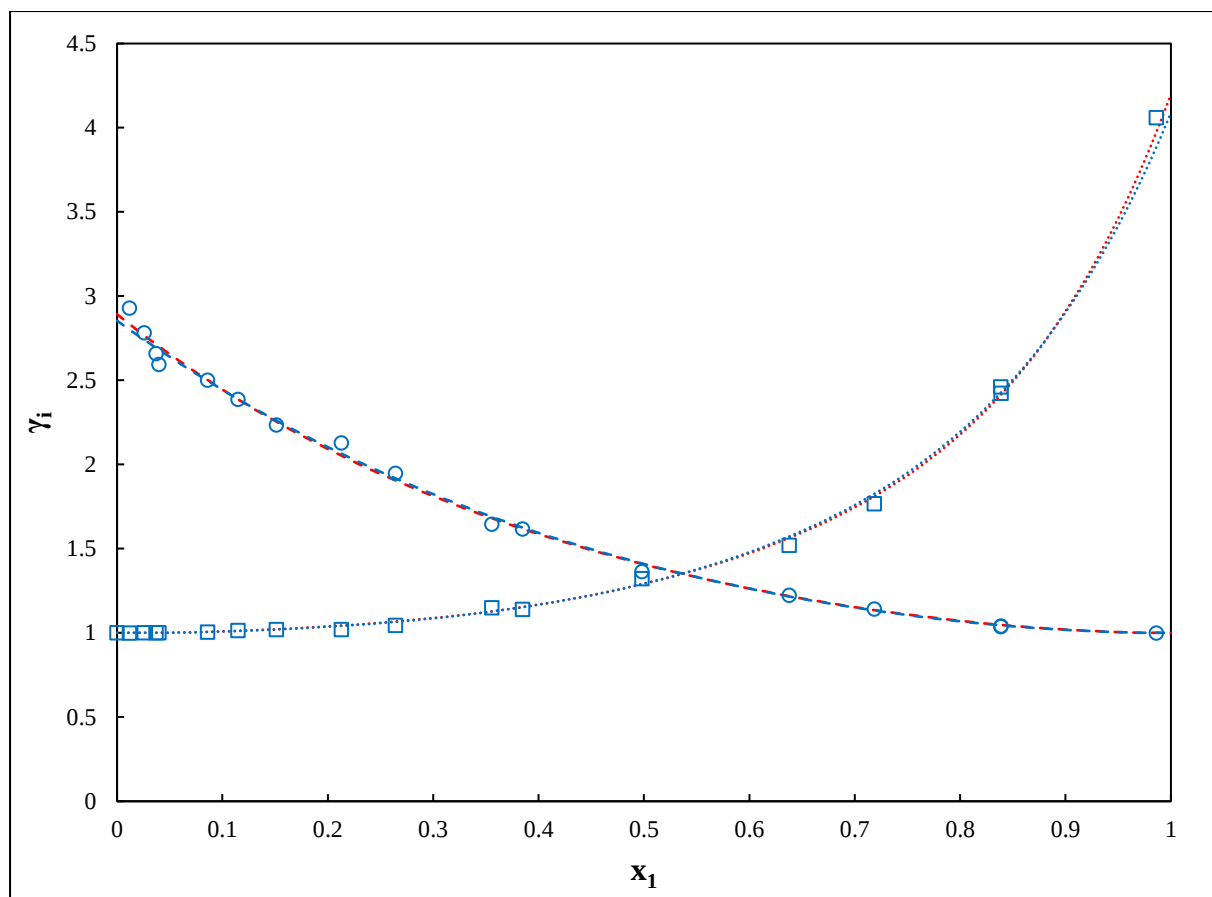


Figure 4.4. γ_i vs. x_1 for the the n-hexane (1) + pentan-2-one (2) system at 313.3 K. γ_1 - x_1 : $\circ$ -experimental, ---, model; γ_2 - x_1 : $\square$ -experimental, --- -model. Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model.

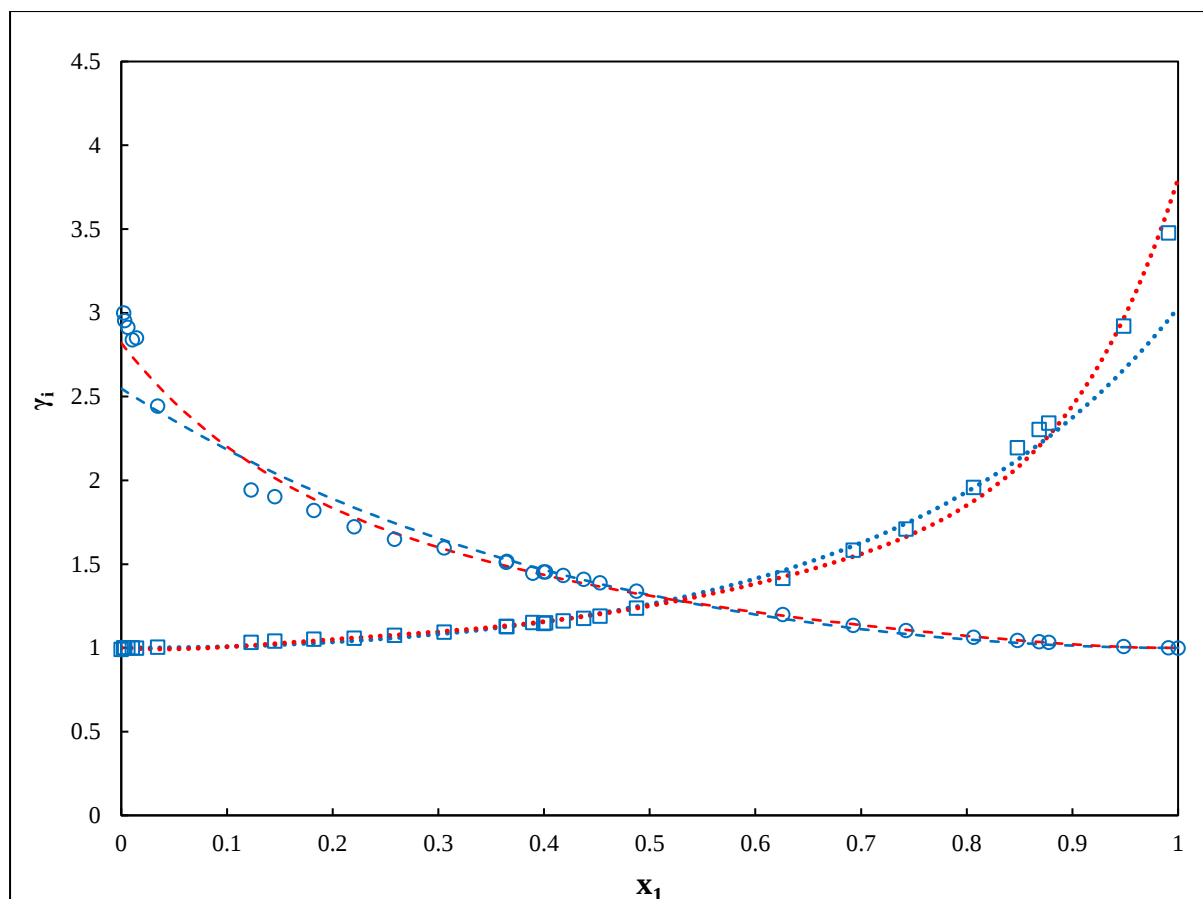


Figure 4.5. γ_i vs. x_1 for the the n-hexane (1) + 4-methylpentan-2-one (2) system at 313.3 K. γ_1 - x_1 : $\circ$ -experimental, - - - model; γ_2 - x_1 : $\square$ -experimental, --- - model. Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model.

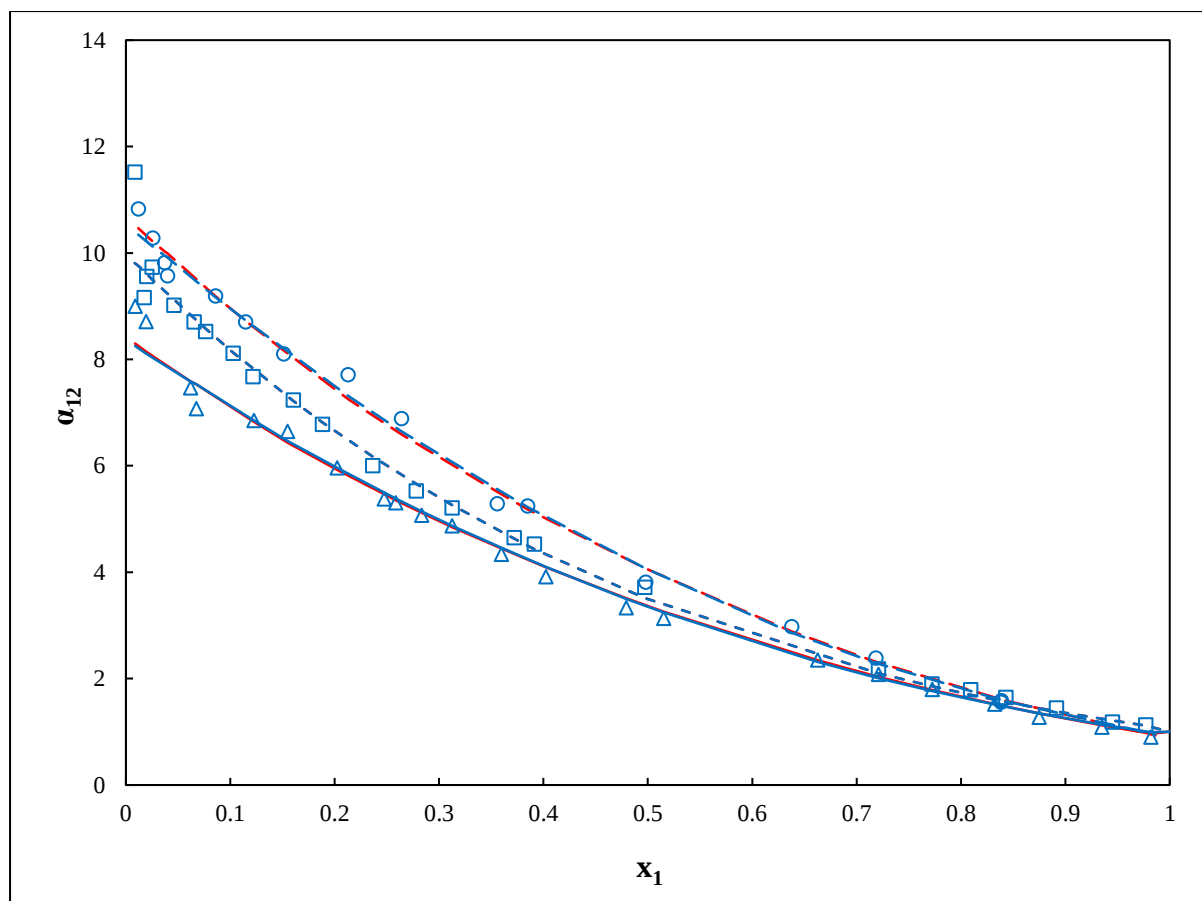


Figure 4.6. α_{12} vs. x_1 for the n-hexane (1) + pentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, ---); 323.3 K, ($\square$, ---); 333.5 K, ($\triangle$, —). Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model.

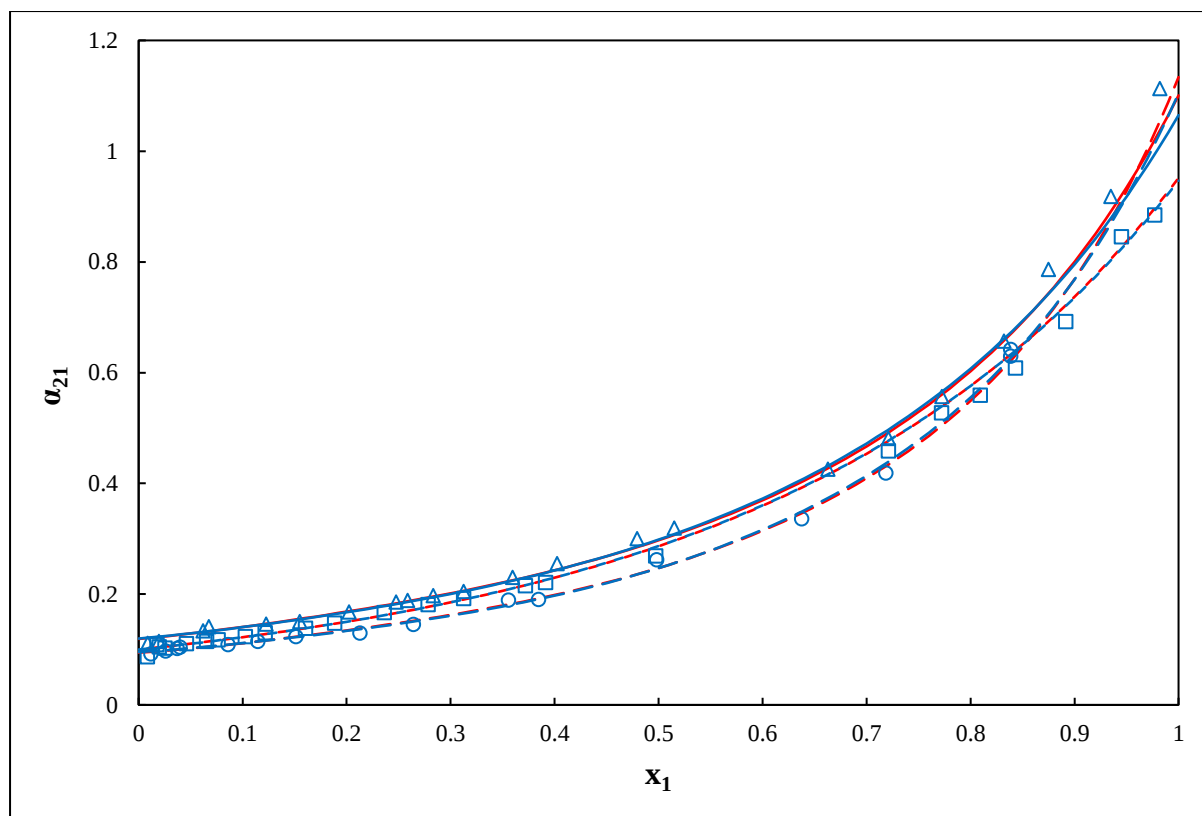


Figure 4.7. α_{21} vs. x_1 for the n-hexane (1) + pentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, ---); 323.3 K, ($\square$, - - -); 333.5 K, ($\triangle$, —). Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model.

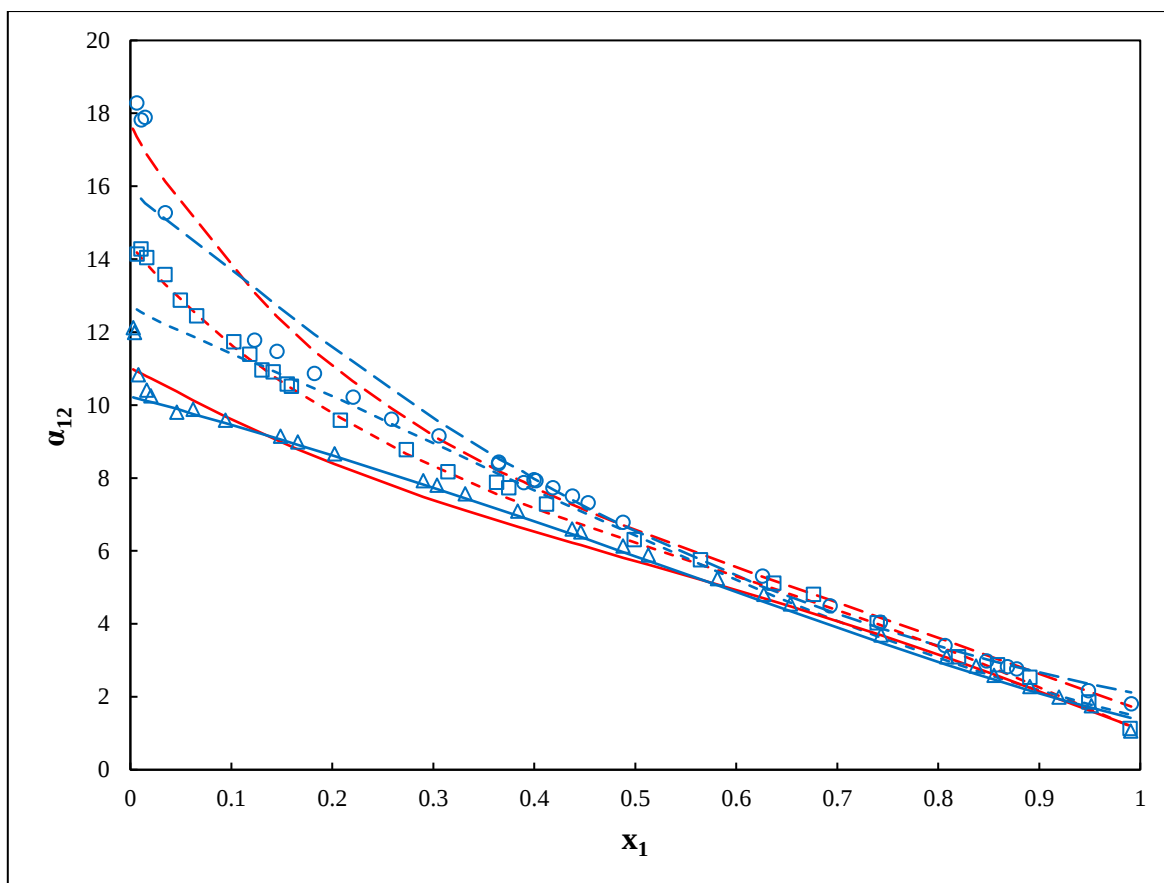


Figure 4.8. α_{12} vs. x_1 for the n-hexane (1) + 4-methylpentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, ---); 323.3 K, ($\square$, - - -); 333.6 K, ($\triangle$, —). Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model.

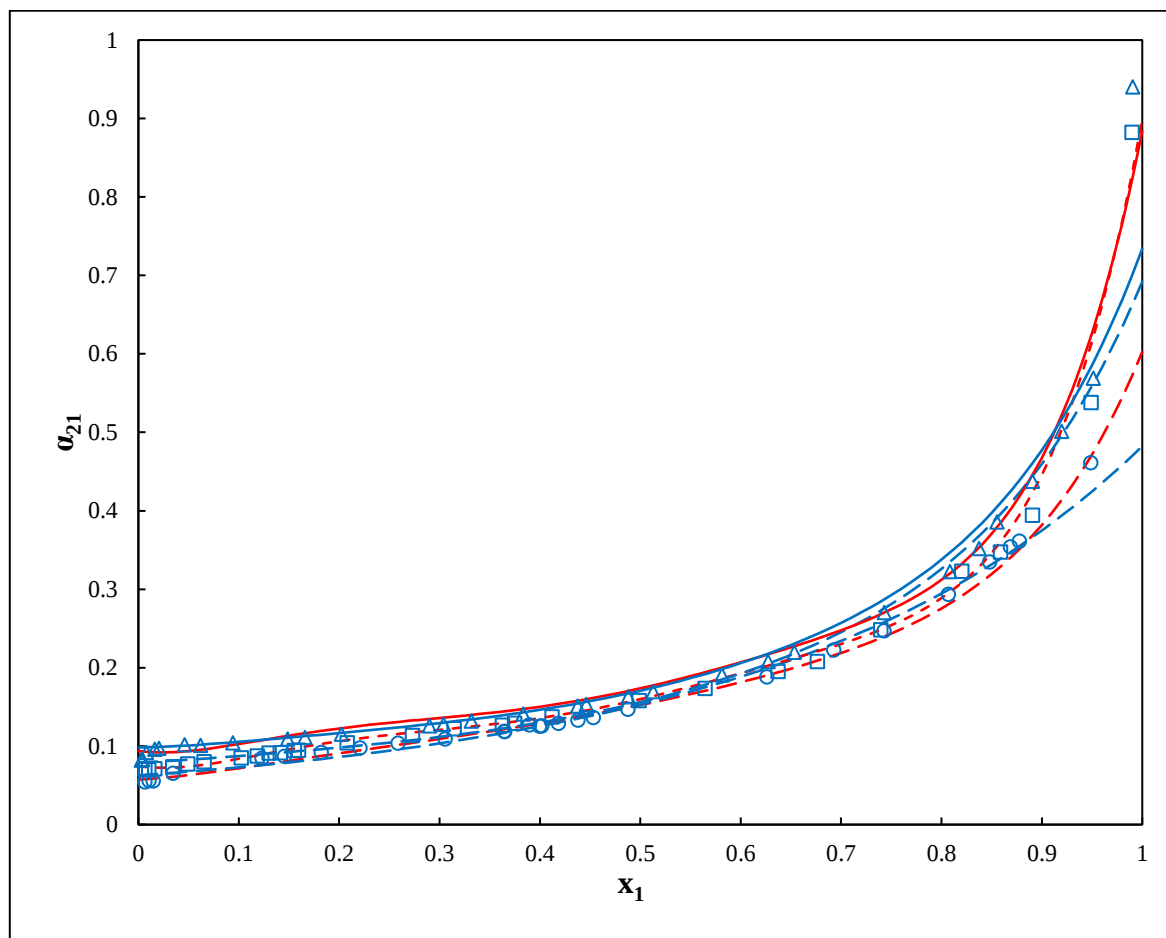


Figure 4.9. α_{21} vs. x_1 for the n-hexane (1) + 4-methylpentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, ---); 323.3 K, ($\square$, - - -); 333.6 K, ($\triangle$, -). Red lines represent the NRTL-HOC model and blue lines are the UNIQUAC-HOC model.

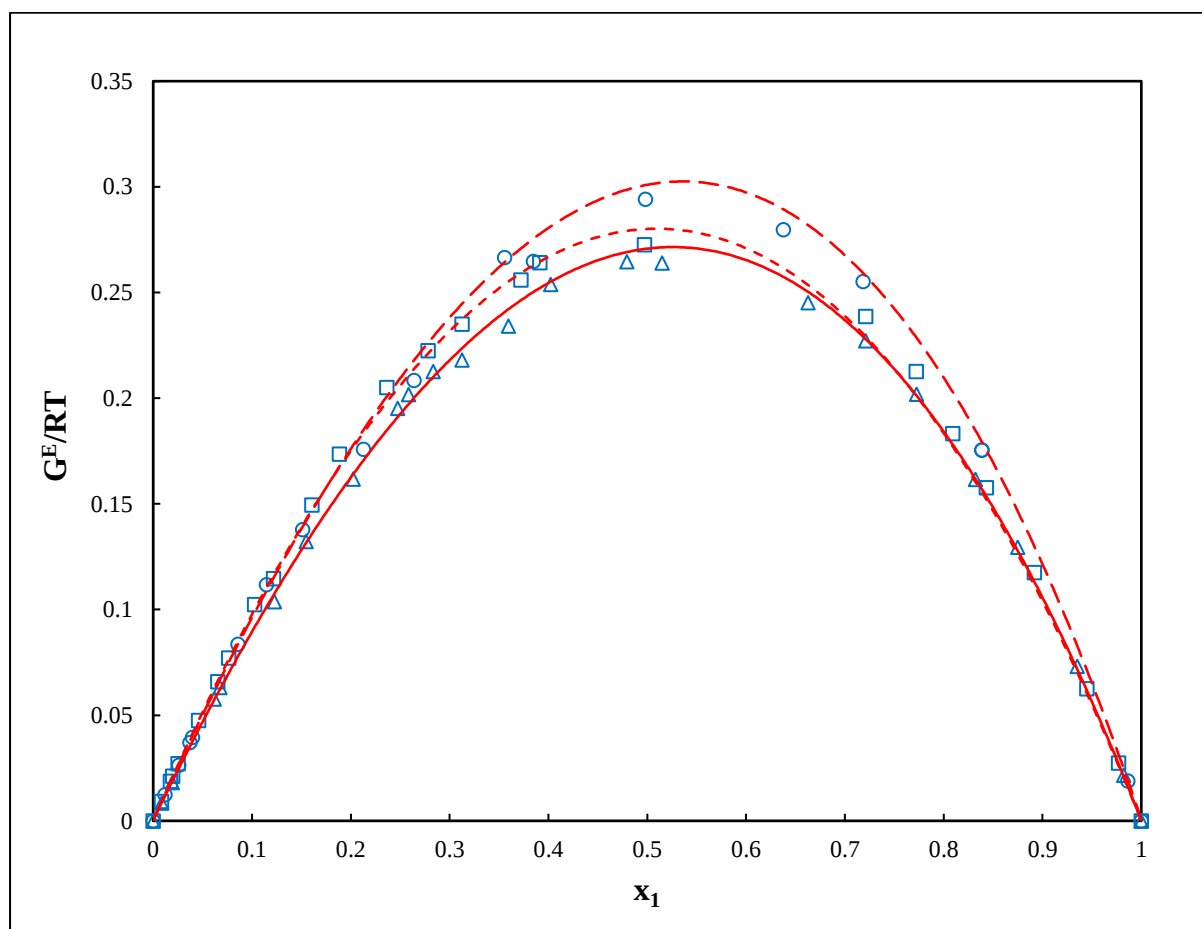


Figure 4.10. $\frac{G^E}{RT}$ vs. x_1 for the n-hexane (1) + pentan-2-one (2) system at: (exp, model):
 313.3 K, ($\circ$, ---); 323.3 K, ($\square$, - - -); 333.5 K, ($\triangle$, —). Red lines represent the
 UNIQUAC -HOC model.

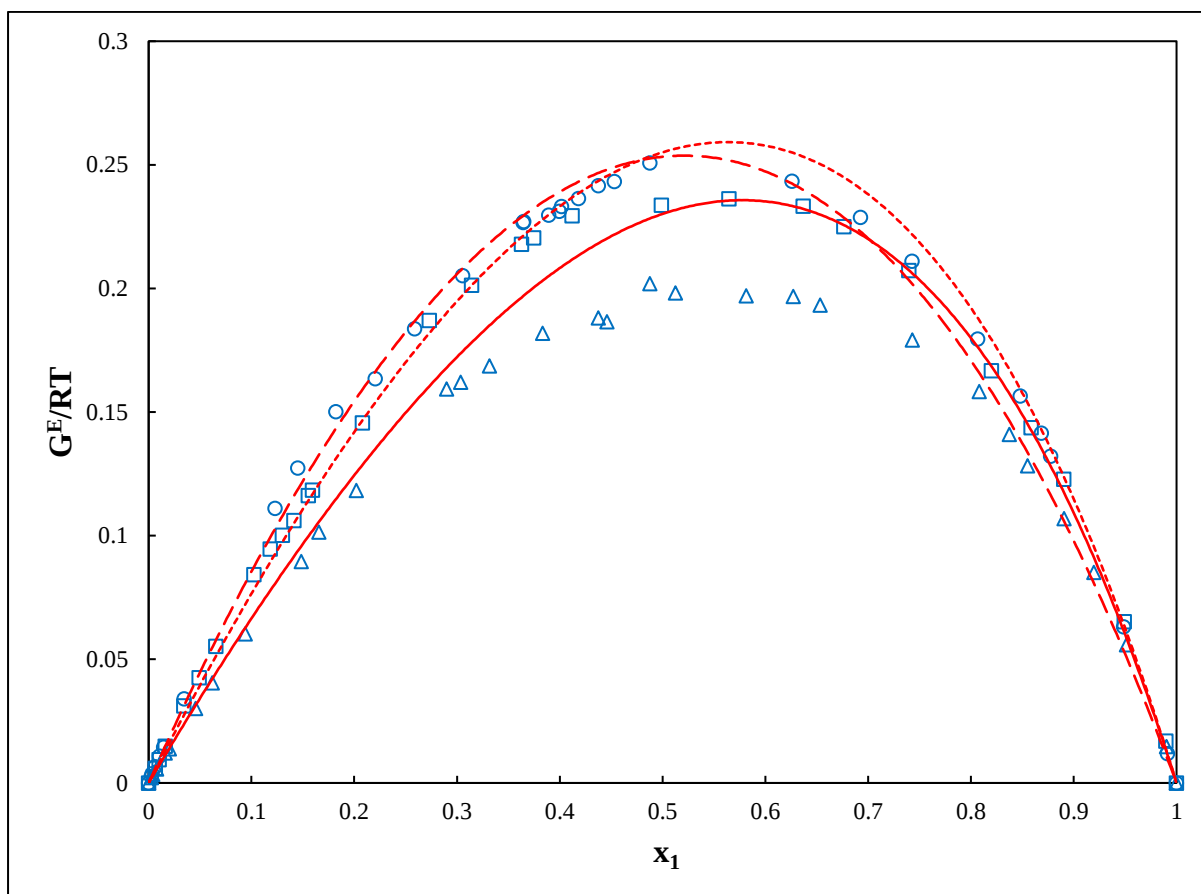


Figure 4.11. $\frac{G^E}{RT}$ vs. x_1 for the n-hexane (1) + 4-methylpentan-2-one (2) system at: (exp, model): ($\circ$, —); 323.3 K, ($\square$, - -); 333.6 K, ($\triangle$, —). Red lines represent the UNIQUAC -HOC model.

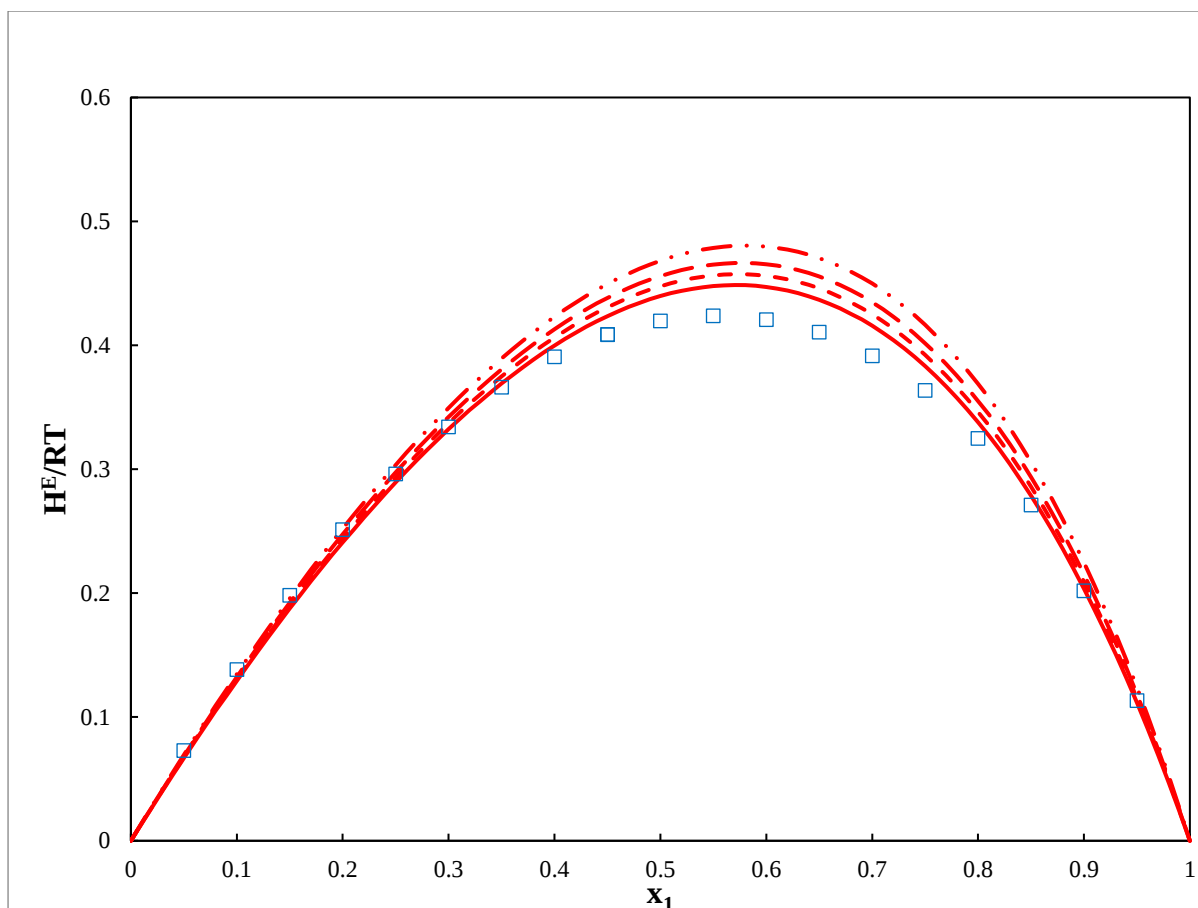


Figure 4.12. $\frac{H^E}{RT}$ vs. x_1 for the n-hexane (1) + pentan-2-one (2) system at: 298.15 K, (exp Kiyohara et al.(Kiyohara et al., 1977), model calculated) ($\square$, $- \cdot -$) and model calculated at: 313.3 K, ($- - -$); 323.3 K, ($- \cdot -$); 333.5 K, ($-$). Red lines represent the UNQUAC-HOC model.

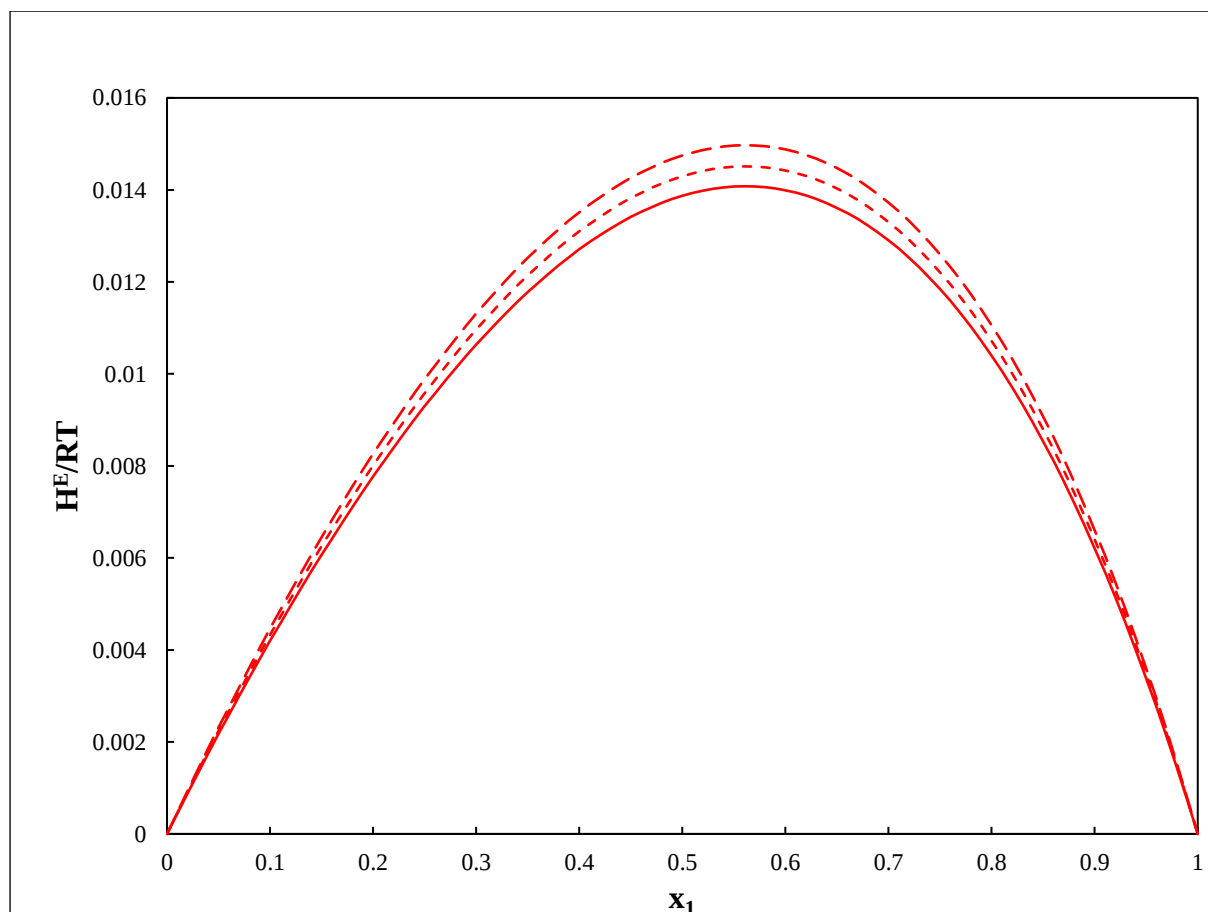


Figure 4.13. $\frac{H^E}{RT}$ vs. x_1 for the n-hexane (1) + 4-methyl pentan-2-one (2) system. model calculated at: 313.3 K, (— — —); 323.3 K, (- - -); 333.6 K, (—). Red lines represent the UNIQUAC-HOC model.

Table 4.10. Pure component parameters used for Peng-Robinson Equation and PC-SAFT models.^a

Component	T_c/K (Poling et al., 2001)	P_c/kPa (Poling et al., 2001)	Ω (Poling et al., 2001)	m	$\sigma/\text{\AA}$	$\frac{\epsilon}{k}/K$
n-hexane	507.60	3025	0.300	3.0576 (Gross and Sadowski, 2001)	3.7983 (Gross and Sadowski, 2001)	236.77 (Gross and Sadowski, 2001)
pentan-2-one	561.10	3690	0.346	3.4304 (Domínguez et al., 2016; Tihic et al., 2006) ^b	3.4688 (Domínguez et al., 2016; Tihic et al., 2006) ^b	249.83 (Domínguez et al., 2016; Tihic et al., 2006) ^b
4-methylpentan-2-one	574.60	3270	0.351	3.3628 (Domínguez et al., 2016; Tihic et al., 2006) ^b	3.6799 (Domínguez et al., 2016; Tihic et al., 2006) ^b	259.89 (Domínguez et al., 2016; Tihic et al., 2006) ^b

^a T_c and P_c are the critical temperature and pressure, ω is the acentric factor. m is the number of segments per chain, σ is the segment diameter, $\frac{\epsilon}{k}$ is the depth of pair potential over the Boltzman constant in the PC-SAFT model.

^b *In lieu* of suitable PC-SAFT parameters in the literature for the ketones, sPC-SAFT(Tihic et al., 2006) (a slight variation of PC-SAFT) parameters were used from the literature(Domínguez et al., 2016; Tihic et al., 2006)

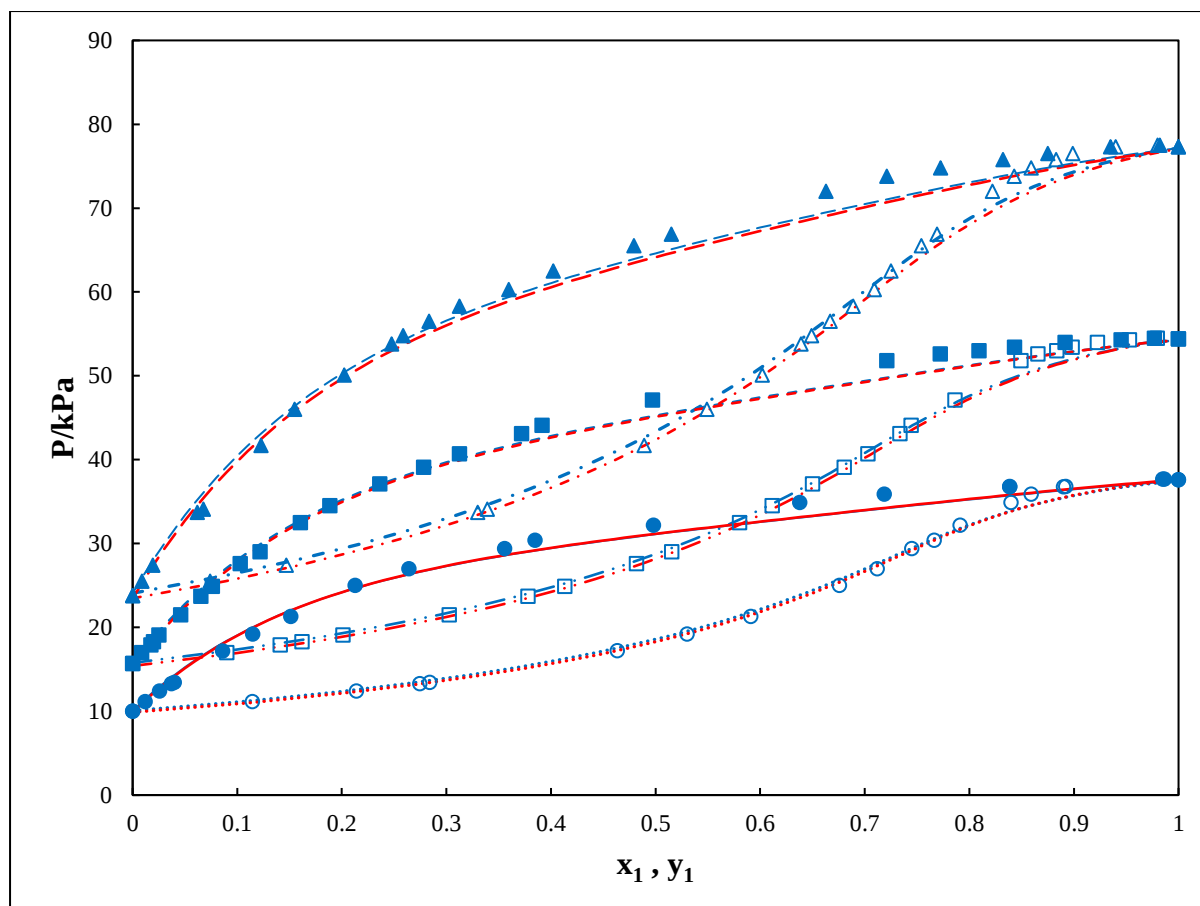


Figure 4.14. Vapour-liquid equilibrium data (P-x-y) for the n-hexane (1) + pentan-2-one (2) system at: (exp. x_1 , exp. y_1 , model x_1 , model y_1): 313.3 K, ($\bullet$, $\circ$, $-$, $\cdots$); 323.3 K, ($\blacksquare$, $\square$, $-$, $\cdots$); 333.5 K, ($\blacktriangle$, $\triangle$, $-$, $\cdots$). Red lines represent the PR model and blue lines represent the PC-SAFT model.

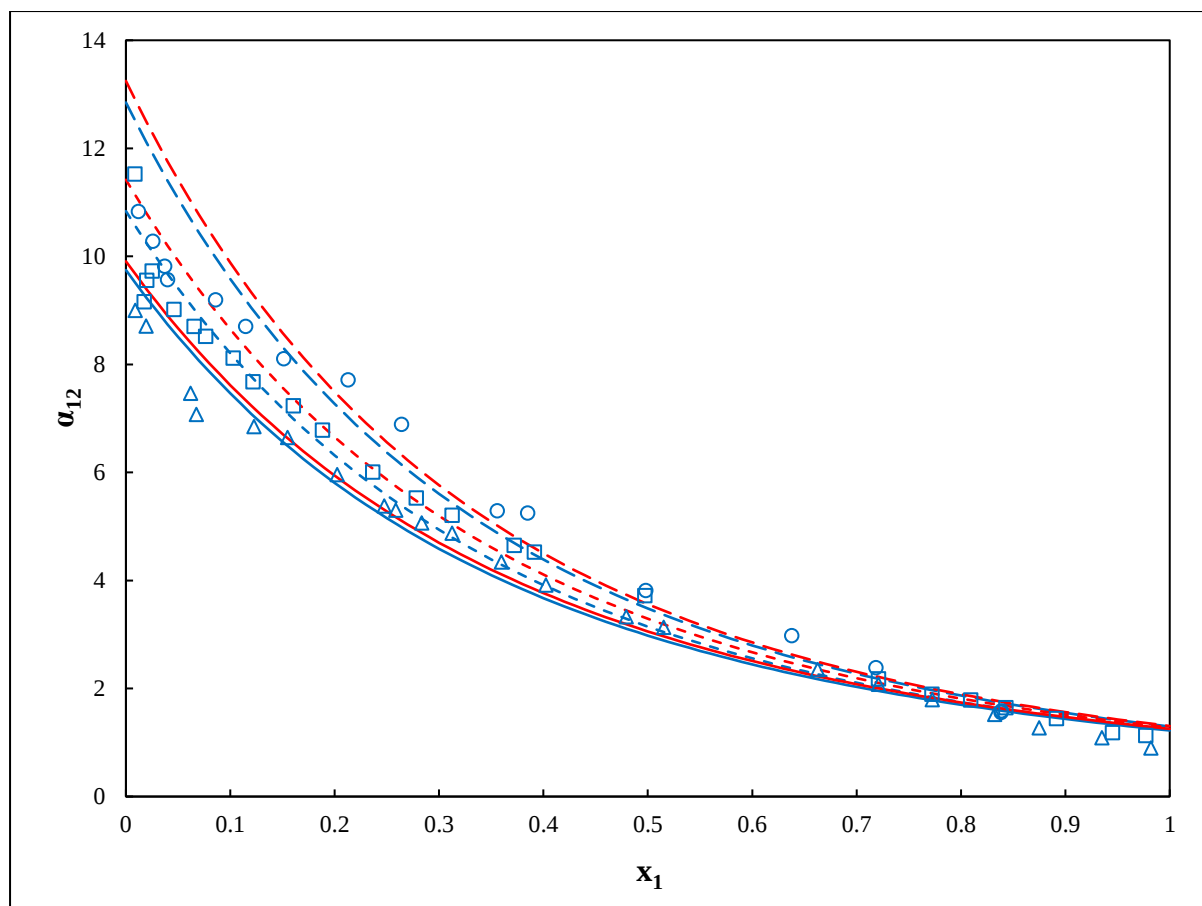


Figure 4.15. α_{12} vs. x_1 for the n-hexane (1) + pentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, — — —); 323.3 K, ($\square$, - - -); 333.5 K, ($\triangle$, —). Red lines represent the PR model and blue lines are the PC-SAFT model.

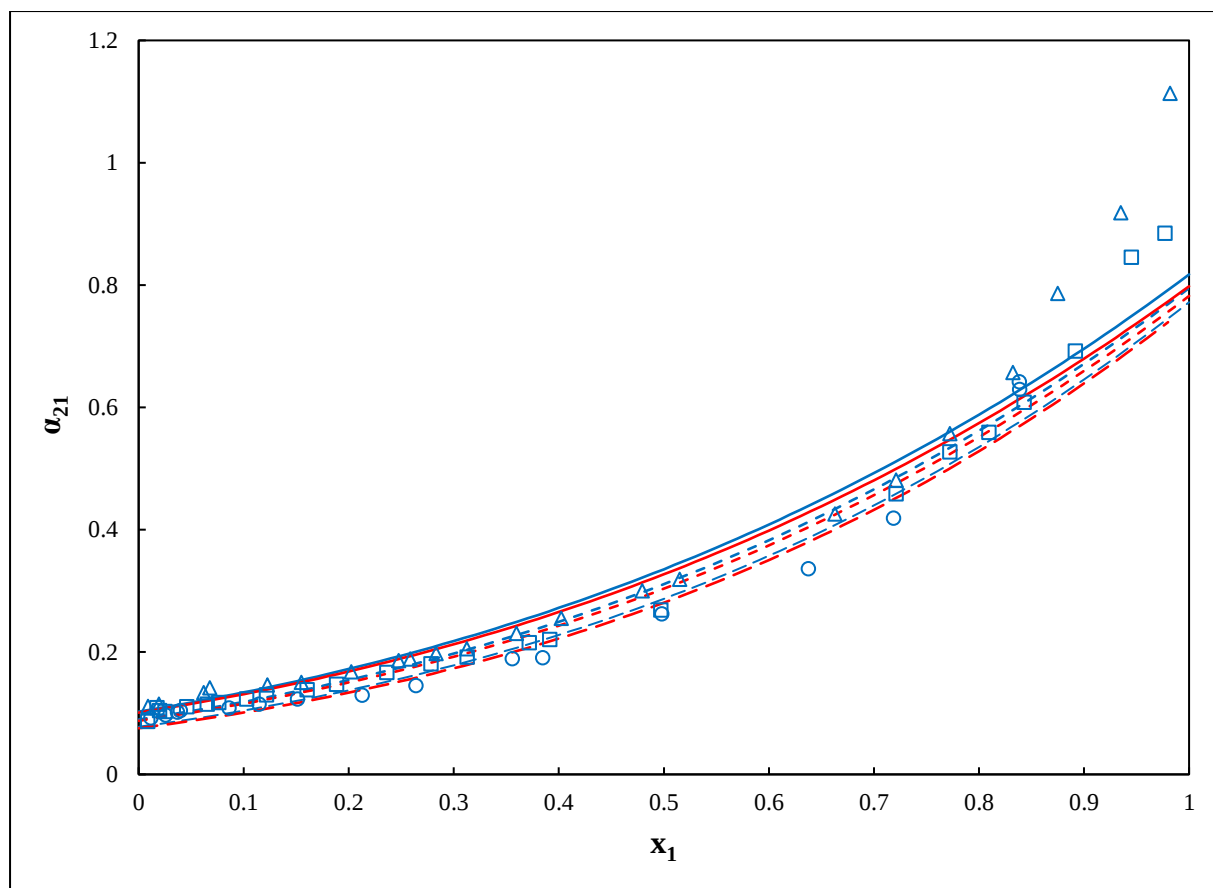


Figure 4.16. a_{21} vs. x_1 for the n-hexane (1) + pentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, — — —); 323.3 K, ($\square$, - - -); 333.5 K, ($\triangle$, —). Red lines represent the PR model and blue lines are the PC-SAFT model.

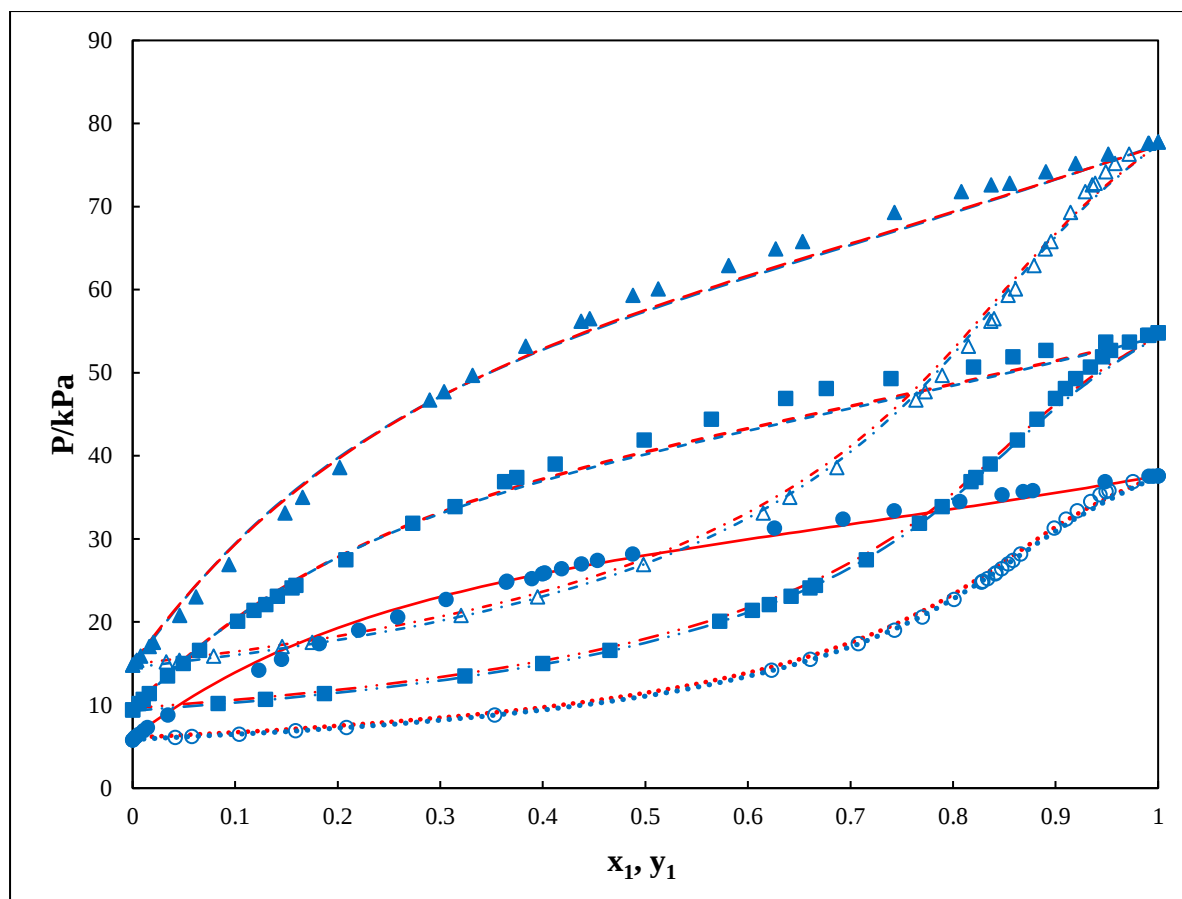


Figure 4.17. Vapour-liquid equilibrium data (P-x-y) for the n-hexane (1) + 4-methylpentan-2-one(2) system at: (exp. x_1 , exp. y_1 , model x_1 , model y_1): 313.3 K, ($\bullet$, $\circ$, —,); 323.3 K, ($\blacksquare$, $\square$, — — —, -.-.); 333.6 K, ($\blacktriangle$, $\triangle$, — — —, -.-.). Red lines represent the PR model and blue lines are the PC-SAFT model.

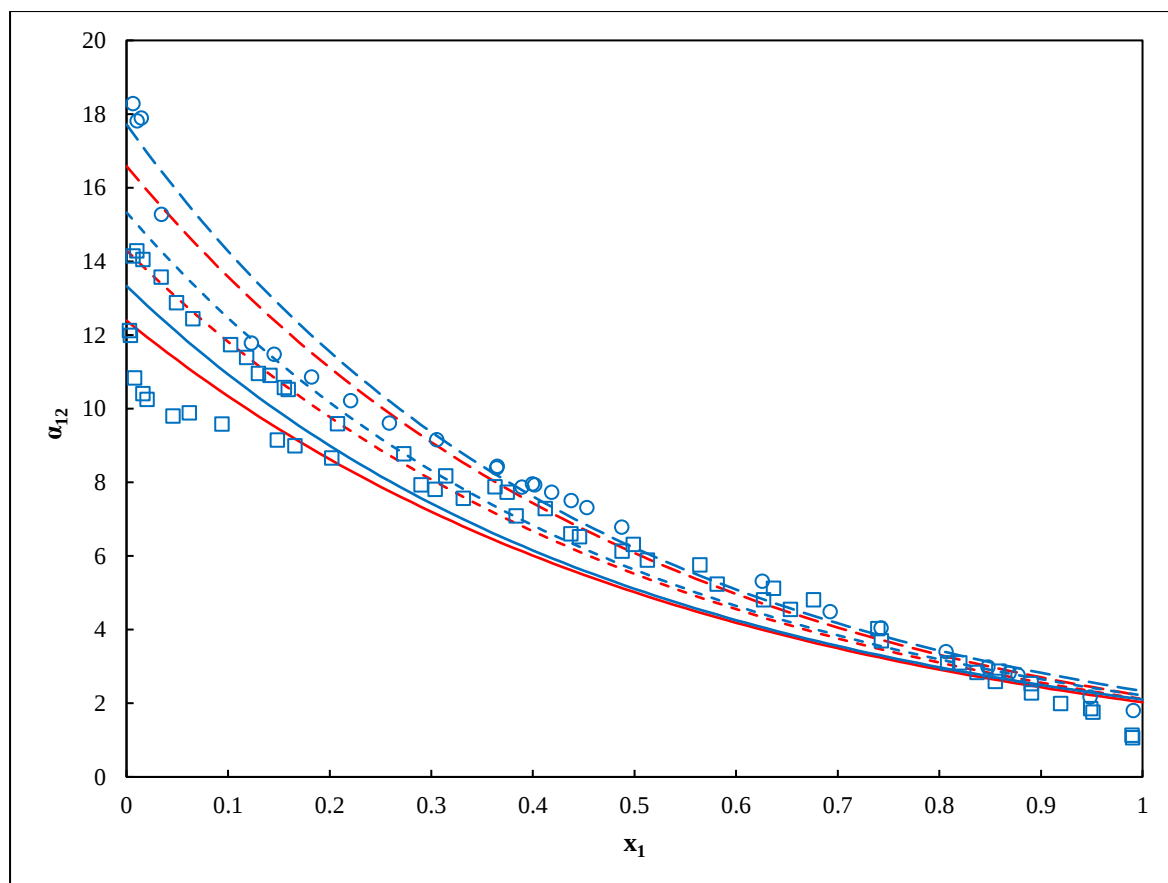


Figure 4.18. a_{12} vs. x_1 for the n-hexane (1) + 4-methylpentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, — —); 323.3 K, ($\square$, - - -); 333.6 K, ($\triangle$, —). Red lines represent the PR model and blue lines are the PC-SAFT model.

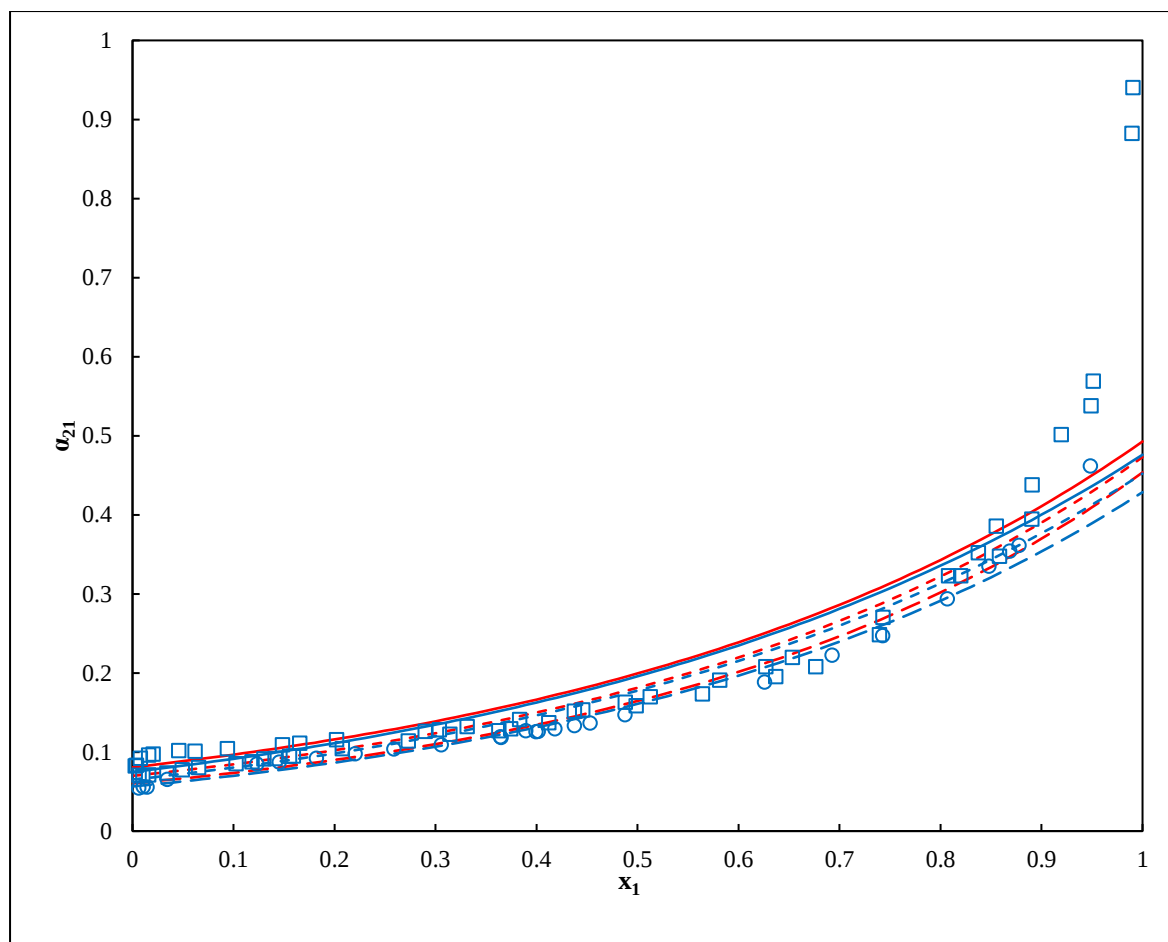


Figure 4.19. α_{21} vs. x_1 for the n-hexane (1) + 4-methylpentan-2-one (2) system at: (exp, model): 313.3 K, ($\circ$, — —); 323.3 K, ($\square$, - - -); 333.6 K, ($\triangle$, —). Red lines represent the PR model and blue lines are the PC-SAFT model.

CHAPTER FIVE

Liquid-Liquid Phase Equilibria for methanol + n-hexane + pentan-2-one/4-methylpentan-2-one at 300-309 K

5.1. Abstract

Liquid-liquid phase equilibrium data were measured for the binary system methanol (1) + n-hexane (2) at approximately (300, 303, 307, 308, 309) K and 0.1 MPa and the ternary systems methanol (1) + n-hexane (2) + pentan-2-one (3) at approximately (300.3, 303.2, 307.3) K and methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) at approximately (303.4, 308.1, 309.0) K and 0.1 MPa. This data informs the blending limits for the mixtures. Experiments were undertaken using a 50cm³ modified doubled-walled glass cell and direct withdrawal of samples for analysis. The experimental tie lines were correlated using the non-random two-liquid (NRTL) and UNIQUAC activity coefficient models. To accomplish this modelling, minimization of the objective function was conducted using nonlinear least-squares via the Aspen Plus ® software. The ternary systems studied were found to exhibit type I ternary LLE behaviour, which indicates a limit to the blending potential of these mixtures as indicated by the heterogenous region measured in this work. Alternatively, if considering separation operations, the relative selectivity of using n-hexane as a solvent to remove pentan-2-one/4-methylpentan-2-one from methanol was found to be greater than unity indicating that it is feasible to use n-hexane for this extraction. Furthermore, the selectivity of n-hexane was found to be more pronounced to pentan-2-one than to 4-methylpentan-2-one.

5.2. Introduction

Ketones, alcohols and alkanes exist in the product and waste stream of the Fischer-Tropsch process (De Klerk, 2008). The separation of these mixtures into pure components are beneficial as they are used in various applications in the petrochemical and solvent industries (Alvarez et al., 2007; Lv et al., 2016; Vázquez-Ojeda et al., 2013) and as feedstock in product development. Phase equilibrium data is necessary to characterize the blending or separation limits/potential of hydrocarbon mixtures with different thermophysical behaviour in process design applications. For example, liquid-liquid extraction and heterogeneous azeotropic distillation are key separation units that are commonly used in industry. Reliable process design for these operations depend on accurate experimental data as predictive methods such as those based on group contribution can often not predict liquid-liquid phase behaviour in ternary systems (Marino et al., 2000). Liquid-liquid extraction is an attractive option for separating alcohol + ketone systems when combined with other oxygenates, and preferred over distillation since it can be carried out under ambient conditions and the energy consumption and environmental impact can be greatly reduced (Fair and Humphrey, 1984; Müller et al., 2008).

Due to the recent regulations imposed on leaded fuel, increasing attention has been given to the further improvement of low octane number (ON) gasoline (Christensen et al., 2011; Goh et al., 2012; Naqvi et al., 2018). Oxygen containing fuel components can be added to fuel blends to obtain a higher-octane quality of unleaded gasoline more easily. Hence, alcohols and ketones can be used as oxygenated additives in unleaded gasoline to improve octane number (Agarwal, 2007). An important consideration for the use of oxygenated compounds in the fuel industry is the separation and blending potential of these fuels with alkanes and alkenes (the main components of petrol and diesel).

Methanol and n-hexane are partially soluble, however the mixtures of methanol or n-hexane with ketones such as pentan-2-one and 4-methylpentan-2-one are completely soluble. These ketones therefore improve the mutual solubility of methanol and n-hexane which is necessary in fuel blending. Alternatively, the experimental LLE phase-characterization of the methanol + n-hexane + ketone systems can also be used to aid the design of the heterogeneous distillation of the methanol-alkane mixture using ketones as the solvent. The data also finds application in the design of liquid-liquid extraction processes and solvent recovery. To design and assess the feasibility of these types of processes, the ternary data for the methanol + n-hexane + ketone

systems are required. In this study, ternary LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at approximately (300.3, 303.2 and 307.3) K and the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at approximately (303.4, 308.1 and 309.0) K and 0.1 MPa were measured. These temperatures were selected for practical and economic purposes such as maintaining process design limits within atmospheric pressure and ambient temperatures, which is common for liquid-liquid extraction operations. Although the temperature range considered seems small, it comprises of a methanol + n-hexane LLE region that has an appreciable change in composition with temperature approaching the upper critical solution temperature, which is not well studied in the literature. Furthermore, ternary LLE data for n-hexane + methanol + pentan-2-one/4-methylpentan-2-one have not been published in the literature to date.

The experimental tie-lines were correlated using the non-random two-liquid (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) activity coefficient models by employing Aspen Plus[®] software. The Othmer-Tobias (Othmer and Tobias, 1942) and Hand (Brandani et al., 1985) equations were used to evaluate the linearity of the data regarding the correspondence of the measured tie-line data.

5.3.Experimental

5.3.1. Materials

The chemicals used in this study were purchased from Sigma-Aldrich[®]. The supplier stated mass purities exceeded 0.99 mass fraction. The purities of all components used in this study were confirmed by using gas chromatograph analysis and refractive index measurements. A Shimadzu GC 2014 equipped with a thermal conductivity detector was used for the sample analysis. The unit was fitted with a POROPAK-Q column (2 m x 2.2 mm) and helium was used as the carrier gas. A detector, column and injector temperature of 513.15 K and a carrier gas flow rate of 30 ml/min were found to be the optimum GC operating conditions for separation of the components. Densities were measured at $T = 298.15$ K using an Anton Paar DSA 5000 apparatus with a supplier-stated accuracy of $0.007 \text{ kg}\cdot\text{m}^{-3}$. Refractive indices of the pure chemicals were determined using an ATAGO RX-7000 α refractometer (sodium D-line = 589 nm) at $T = 293.15$ K. The supplier uncertainty was 0.0001. An MKS 500 device was employed to perform Karl Fischer titration on the ketones and methanol to determine the water content

and was found to be below 0.0005 mass fraction. The purities and chemical suppliers are provided in Table 5.1.

5.3.2. Equipment and uncertainties

The modified doubled-walled sealable glass cell of Raal and Brouckaert (1992) commissioned by Ndlovu (2005) was used to conduct the LLE measurements by employing the direct analytical method. The experimental procedure used followed the method described by Alders (1959). A schematic of the cell is shown in Figure 5.1. A teflon coated magnetic stirrer bar was placed inside the 50cm³ equilibrium cell and a stirrer plate was used to induce mixing. The stirrer was set at a moderate speed to prevent emulsions from forming and the cell contents were allowed to stir for approximately 8 hours to reach thermal equilibrium. The stirrer was then switched off and contents left to settle for 12 hours. This was followed by the removal of 1µl samples of the top and bottom phases of the cell and analysed using the gas chromatograph. A minimum of three samples were performed for each phase composition to obtain a repeatability with relative difference below 1% in composition. The stirring and equilibrium times were determined at the onset of experiments by trial and error, by ensuring further changes in sample composition did not occur after subsequent sampling beyond the selected equilibration time.

Being double-walled, the temperature of the cells were controlled by the flow of fluid through the jacket from a thermostated oil bath. The cell lid contains an isolated thermal well in which a temperature sensor was placed. A Pt-100 class-A temperature sensor was alternated between the oil bath and the cell lid thermowell to confirm that temperature gradients did not occur along the lines and cell. This probe was used to determine the equilibrium temperature and was calibrated using a WIKA CTB 9100 temperature standard. The standard combined uncertainty in temperature was calculated to be 0.1 K. The atmospheric pressure was obtained from a WIKA CPC 6000 pressure standard with display, with a standard combined uncertainty of 1 kPa.

The area ratio method of Raal and Mühlbauer (1998) was used to calibrate the GC detector. The mixtures for the calibration were prepared gravimetrically using acetone as an internal standard to homogenize the methanol + n-hexane mixture. A Mettler-Toledo mass balance (model AB204-S) with an uncertainty of 0.0001g was used to weigh and prepare the mixtures.

The standard combined uncertainty in composition was calculated to be 0.005 mole fraction. For all uncertainty calculations, procedures outlined by NIST JCGM (ISO, 2008) were followed. The combined uncertainties were calculated by type A and type B propagation of errors and took into account the supplier uncertainty, uncertainty from calibration, uncertainty from repeatability and the uncertainty introduced by chemical impurity in the relevant calculations.

5.4. Results and Discussion

A test system of methanol (1) + n-hexane (2) was measured to verify the experimental technique, and the data is presented and compared to literature data in Figure 5.2. A good correlation within experimental uncertainty in temperature and composition is observed for at least one literature source (Blanco and Ortega, 1996), for the majority of the composition range. This literature data was measured by cloud point method, with a stated composition precision of 0.0002 mole fraction and temperature precision of 0.01 K. The tie-line data of Orge et al. (1997) was analysed by refractive index, which can sometimes produce non-linear trends with composition in alcohol + alkane mixtures, resulting in low composition precisions. This may account for the discrepancies from this study. The upper critical solution temperature for the mixture is within the limits of the two available literature sources, and also agrees with proprietary literature data for this system reported in the study of Orge et al. Unfortunately, the additional proprietary data is not available in the open literature for graphical comparison here.

The experimental and modelled LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (300.3, 303.2 and 307.3) K and the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at (303.4, 308.1 and 309.0) K and 0.1 MPa are provided in Tables 5.2 and 5.3 and plotted on ternary diagrams in Figures 5.3 to 5.16.

In both systems it can be seen that temperature has an effect on the size of the phase envelop. The width and height of the phase envelope decreases with increasing temperature. For all three temperatures, the region of immiscibility is relatively small for the ternary system and is approximately between $x_1 = 0.27$ to $x_1 = 0.79$, $x_2 = 0.20$ to $x_2 = 0.73$ and $x_3 = 0$ to $x_3 = 0.25$ for the methanol (1) + n-hexane (2) + pentan-2-one (3) system and between $x_1 = 0.33$ to $x_1 = 0.74$, $x_2 = 0.25$ to $x_2 = 0.67$ and $x_3 = 0$ to $x_3 = 0.1$ for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system.

The theoretical models and approach applied in this work have been reviewed extensively (Brijmohan and Narasigadu, 2020; Narasigadu et al., 2009; Walas, 2013). For this work, the non-random two liquid (NRTL) (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) activity coefficient models were used to correlate the experimental tie-lines using non-linear least-squares regression on ASPEN Plus® Version 10 software by applying the Britt–Leucke algorithm and Deming Initialisation method (Britt and Luecke, 1973). The correlated NRTL and UNIQUAC model parameters are reported in Tables 5.4 and 5.5. The minimization of the objective function by non-linear least-squares was chosen over the maximum-likelihood method, which has been recommended in the literature (Narasigadu et al., 2009; Novák, J.P., Matouš, J. and Pick et al., 1987). The non-randomness parameter of the NRTL model (α_{ij}) was fixed at 0.2 for all three binary pairs which is in the range of values suggested by Walas (Walas, 2013). Attempts were made to regress α_{ij} , but these results provided a poor correlation of the experimental data. Similarly, a reasonable single set of temperature dependent model parameters for each system was not found, hence each system and temperature were modelled individually.

To determine the performance of each model, the root mean square deviation (RMSD) was calculated and reported in the tables.

$$RMSD = \left(\frac{\sum_1^N \sum_\alpha \pi_\alpha \sum_i^2 (x_i^{\alpha exp} - x_i^{\alpha calc})^2}{6N} \right)^{1/2} \quad (5.1)$$

where x is the liquid phase mole fraction, N is the number of experimental points, and π and α are the two phases.

Both the NRTL and UNIQUAC models provide a satisfactory correlation of the experimental data within the experimental uncertainty. However, the RMSD values shown in Tables 5.4 and 5.5 indicate that the NRTL model generally provides a better representation of the experimental data with RMSD values between 0.0001 and 0.002 for the NRTL model and between 0.0002 and 0.015 for the UNIQUAC model. The largest deviation was observed for modelling of the methanol (1) + n-hexane (2) + pentan-2-one (3) system at 300.3 K using the UNIQUAC model. This may be attributed to this system exhibiting the largest miscibility gap, with a steep change in the tie-line data between the binary and ternary points. There is no significant difference in

the shape of the graphical representation of the LLE phase behaviour between the two ternary systems considered. Both systems are seen to exhibit type I ternary LLE behaviour at all temperatures. A type 1 system suggests that the solutes and solvent are completely miscible in the temperature range considered. The region of immiscibility is larger in the methanol (1) + n-hexane (2) + pentan-2-one (3) systems at equivalent temperatures. This indicates that 4-methylpentan-2-one (3) is able to homogenize the methanol - n-hexane mixture to a greater extent than pentan-2-one, which is useful for blending purposes. This may be attributed to the additional alkyl group on the 4-methylpentan-2-one molecule which possibly allows for improved attraction of the non-polar n-hexane molecules, while maintaining the polar association with the alcohol group on the methanol molecules. This additional non-polar site is not available on the pentan-2-one molecule. Thus, reducing its homogenising properties. Alternatively, if one considers the separation of the binary methanol-n-hexane heterogenous azeotrope, at 0.5 mole fraction (1 atm), the results from this study show the potential of a ketone solvent. The ketones considered in this work can be used to effectively separate the methanol-n-hexane azeotrope by a heterogenous distillation operation. This is discussed further in the following chapter.

Solvent selection for liquid-liquid extraction is an important design consideration as it directly affects process efficiency. The use of n-hexane as the solvent in a liquid-liquid extraction operation aids the separation of ketone-methanol mixtures to valorise either the ketones or methanol. Relative selectivity (β) is a parameter used to measure the effectiveness of a solvent (Walas, 2013). A solvent would be regarded effective if the relative selectivity, β , exceeds a value of 1.

For methanol as the carrier (1), n-hexane as the solvent (2), and pentan-2-one/4-methylpentan-2-one as the solute (3), β is defined as:

$$\beta = \frac{\frac{x_3^{II}}{x_1^{II}}}{\frac{x_3^I}{x_1^I}} \quad (5.2)$$

where *I* and *II* represent the n-hexane-dilute phase and the n-hexane-rich phase respectively. In Tables 5.2 and 5.3 the relative selectivity (β) is presented, and is shown to be greater than unity, implying that n-hexane is effective in removing pentan-2-one/4-methylpentan-2-one

from methanol mixtures. Additionally, n-hexane is significantly more selective (up to three-fold in some instances) to pentan-2-one than 4-methylpentan-2-one. Note that heavier n-alkanes such as n-heptane or n-octane would likely serve as better extraction solvents for the proposed LLE separation as they are significantly less miscible with methanol than n-hexane. However, the data presented here, with the characteristic interactions, are useful for the design and modelling of applications where mixed n-alkane extraction solvents are employed.

The tie lines have a negative slope toward methanol and the gradient of the lines gets steeper as the composition of the ketone increases until the plait point is reached. Plait points were estimated by the intermediate point method (Mangiapia et al., 2016) and are provided in Table 5.6. Linearity testing of the experimental LLE data can be used to evaluate the relative reliability of the individual tie-lines by correlating the data using the Othmer and Tobias (1942) and Hand (Brandani et al., 1985) equations. Carniti et al. (1978) showed that the linearity of these correlations cannot be used to confirm any “consistency” of LLE data, however they can be used to evaluate the reliability of a particular tie-line for a system in comparison to the others.

The Othmer-Tobias correlation is given by:

$$\ln \left[\frac{(1-x_3^{\text{II}})}{x_3^{\text{II}}} \right] = a + b \ln \left[\frac{(1-x_1^{\text{I}})}{x_1^{\text{I}}} \right] \quad (5.3)$$

and the Hand correlation is given by:

$$\ln \left[\frac{(x_2^{\text{II}})}{x_3^{\text{II}}} \right] = c + d \ln \left[\frac{(x_2^{\text{I}})}{x_1^{\text{I}}} \right] \quad (5.4)$$

Where a , b , c , d are the fitting constants for the Othmer-Tobias and Hand equations, x_2^{II} and x_3^{II} are the mole fractions of n-hexane and pentan-2-one/4-methylpentan-2-one in the methanol-dilute phase respectively, and x_1^{I} and x_2^{I} are the mole fractions of methanol and n-hexane in the methanol-rich phase. The Othmer-Tobias and Hand plots are shown in Figures 5.17 to 5.20. The results for both systems show a reasonable linear behaviour of $R^2 \geq 0.96$ which indicates that the measured tie-line data follow the expected trend given by equations 5.3 and 5.4. It was however found that the tie lines for the methanol (1) + n-hexane (2) + pentan-

2-one (3) system at (300.3 K and $x_1^I = 0.772$, $x_1^{II} = 0.276$) and at (303.2 K and $x_1^I = 0.739$ and $x_1^{II} = 0.331$) did not conform to a linear trend with the other tie-lines according to equations 5.3 and 5.4. This was attributed to the significant gradient change in the tie-lines in this region, from the respective horizontal binary tie-line.

5.5. Conclusion

Liquid-liquid equilibrium data for the ternary systems of methanol + n-hexane + pentan-2-one/4-methylpentan-2-one were successfully measured with compositions of the tie line end points reported. All systems studied were found to exhibit type I ternary LLE behaviour and the NRTL and UNIQUAC thermodynamic models provided an acceptable correlation to the experimental data. The root mean square deviations (RMSD) were within the experimental uncertainty for the NRTL model, and between 0.0001 and 0.002 while the UNIQUAC model reported deviations of 0.0002 to 0.015 with the highest deviation found in the methanol (1) + n-hexane (2) + pentan-2-one using the UNIQUAC model. The relative selectivities for all systems were in the range of 1.23-6.41. It can be concluded that the extraction of ketones from methanol using n-hexane is feasible with n-hexane having a larger relative selectivity to pentan-2-one than 4-methylpentan-2-one. The Othmer-Tobias and Hand correlation plots indicated the consistency in the measured LLE tie-lines. The potential use of these results can enable separation of the heterogeneous methanol-n-hexane azeotrope.

Table 5.1. Details of chemicals used in this study.

Component ^a	CAS RN.	Refractive index (RI) at 293.15 K and 0.101 MPa. ^b		Density (kg.m ⁻³) ^d		Minimum mass fraction purity ^e	GC peak relative area (mass fraction purity)
		Exp.	Lit. ^c	Exp.	Lit.		
n-hexane	110-54-3	1.3750	1.3750	655.02	654.9	≥0.990	0.999
					(Sastrey and Valand, 1998)		
					655.3 (Fang et al., 2008)		
pentan-2-one	107-87-9	1.3899	1.3895	801.75	801.42	≥0.995	0.999
					(González et al., 2005)		
					801.91 (Domańska et al., 2002)		
4-methylpentan-2-one	108-10-1	1.3961	1.3962	795.98	795.94	≥0.990	0.999
					(Lladosa et al., 2011)		
					796.03 (Marrufo et al., 2011)		
methanol	67-56-1	1.3291	1.3288	786.77	786.86	≥0.995	0.998
					(Diaz Peña and Tardajos, 1979) ^v		
					786.55 (Sun et al., 1988)		

^aAll chemicals were supplied by Sigma Aldrich with stated purities^bStandard combined uncertainties u_c are $u_c(RI) = 0.0001$ and standard uncertainties u are $u(T) = 0.1 K$, $u(P) = 0.1 kPa$ ^cHaynes at 293.15 K^dDensity measured at 298.15 K and 0.101 MPa. Standard uncertainties u are $u(\rho) = 0.2 \text{ kg.m}^{-3}$, $u(T) = 0.01 K$, $u(P) = 0.1 kPa$,^eAs stated by supplier

Table 5.2. Experimental liquid-liquid equilibrium data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (300.3, 303.2 and 307.3) K and 0.1 MPa.^a

Lower phase (I)			Upper phase (II)			
x_1	x_2	x_3	x_1	x_2	x_3	β
$T = 300.3 \text{ K}$						
0.538	0.243	0.219	0.425	0.324	0.251	1.45
0.569	0.233	0.198	0.362	0.413	0.225	1.79
0.613	0.221	0.166	0.321	0.490	0.189	2.17
0.646	0.222	0.133	0.304	0.542	0.154	2.46
0.685	0.215	0.100	0.289	0.592	0.119	2.82
0.730	0.209	0.062	0.282	0.624	0.094	3.92
0.772	0.204	0.024	0.276	0.669	0.055	6.41
0.790	0.210	0.000	0.271	0.729	0.000	
$T = 303.2 \text{ K}$						
0.548	0.274	0.178	0.428	0.371	0.201	1.45
0.593	0.263	0.145	0.391	0.433	0.176	1.84
0.624	0.254	0.122	0.365	0.483	0.152	2.13
0.652	0.252	0.096	0.355	0.517	0.128	2.45
0.676	0.249	0.075	0.347	0.550	0.103	2.68
0.702	0.243	0.055	0.339	0.580	0.081	3.05
0.739	0.238	0.023	0.331	0.633	0.037	3.59
0.758	0.243	0.000	0.321	0.679	0.000	
$T = 307.3 \text{ K}$						
0.546	0.343	0.112	0.471	0.380	0.149	1.54
0.562	0.339	0.099	0.441	0.427	0.132	1.70
0.582	0.337	0.081	0.433	0.461	0.106	1.76
0.598	0.336	0.066	0.430	0.478	0.093	1.96
0.613	0.335	0.052	0.425	0.500	0.075	2.08
0.639	0.331	0.031	0.424	0.527	0.049	2.38
0.658	0.331	0.011	0.423	0.558	0.019	2.69
0.668	0.332	0.000	0.428	0.572	0.000	

^a Standard combined uncertainties u_c are $u_c(T) = 0.1 \text{ K}$, $u_c(P) = 1 \text{ kPa}$, $u_c(x_i) = 0.005$

Table 5.3. Experimental liquid-liquid equilibrium data for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at (303.4, 308.1 and 309.0) K and 0.1 MPa.^a

Lower phase (I)			Upper phase (II)			
x_1	x_2	x_3	x_1	x_2	x_3	β
$T = 303.4$ K						
0.623	0.310	0.068	0.400	0.519	0.081	1.86
0.644	0.302	0.054	0.387	0.549	0.064	1.97
0.668	0.290	0.042	0.381	0.569	0.050	2.09
0.685	0.281	0.034	0.368	0.591	0.041	2.24
0.711	0.267	0.022	0.360	0.612	0.028	2.51
0.723	0.261	0.016	0.354	0.626	0.020	2.55
0.731	0.257	0.012	0.349	0.635	0.016	2.79
0.746	0.254	0.000	0.333	0.667	0.000	
$T = 308.1$ K						
0.564	0.382	0.054	0.518	0.421	0.061	1.23
0.569	0.380	0.051	0.503	0.440	0.057	1.26
0.574	0.379	0.047	0.499	0.448	0.053	1.30
0.581	0.376	0.043	0.491	0.461	0.048	1.32
0.590	0.373	0.037	0.484	0.475	0.041	1.35
0.619	0.363	0.018	0.471	0.508	0.021	1.53
0.632	0.358	0.010	0.469	0.518	0.013	1.75
0.644	0.356	0.000	0.463	0.537	0.000	
$T = 309.0$ K						
0.556	0.421	0.023	0.506	0.469	0.026	1.24
0.568	0.417	0.015	0.498	0.484	0.018	1.37
0.575	0.413	0.012	0.497	0.489	0.014	1.35
0.581	0.410	0.009	0.496	0.494	0.011	1.43
0.585	0.409	0.007	0.494	0.498	0.009	1.52
0.592	0.404	0.004	0.493	0.502	0.005	1.50
0.603	0.397	0.000	0.492	0.507	0.000	
^a Standard combined uncertainties u_c are $u_c(T) = 0.1$ K, $u_c(P) = 1$ kPa, $u_c(x_i) = 0.005$						

^a Standard combined uncertainties u_c are $u_c(T) = 0.1$ K, $u_c(P) = 1$ kPa, $u_c(x_i) = 0.005$

Table 5.4. NRTL and UNIQUAC interaction parameters and root mean square deviations (RMSD) for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (300.3, 303.2 and 307.3) K and 0.1 MPa.

Parameter	Model	
	$T = 300.3 \text{ K}$	
	NRTL ^b	UNIQUAC ^c
a_{12}	1.947	0.010
a_{21}	0.638	0.014
a_{13}	4.562	0.762
a_{31}	-0.385	-0.226
a_{23}	3.111	1.724
a_{32}	21.218	-0.423
$\alpha_{ij,NRTL}$	0.2	-
RMSD ^a	0.002	0.015
$T = 303.2 \text{ K}$		
	NRTL ^b	UNIQUAC ^c
a_{12}	1.547	-0.016
a_{21}	15.168	-0.013
a_{13}	3.372	0.298
a_{31}	0.571	0.390
a_{23}	1.969	0.914
a_{32}	5.200	1.278
$\alpha_{ij,NRTL}$	0.2	-
RMSD ^a	0.001	0.010
$T = 307.3 \text{ K}$		
	NRTL ^b	UNIQUAC ^c
a_{12}	3.645	0.223
a_{21}	-0.289	0.032
a_{13}	5.600	-0.043
a_{31}	-0.455	0.611
a_{23}	1.685	0.463
a_{32}	11.748	0.619
$\alpha_{ij,NRTL}$	0.2	-
RMSD ^a	0.001	0.002

$$^a \text{RMSD} = \left(\frac{\sum_1^N \sum_{\alpha} \pi_{\alpha} \sum_i^2 (x_i^{\alpha \text{exp}} - x_i^{\alpha \text{calc}})^2}{6N} \right)^{1/2}$$

Model parameters can be related to those described in the original works by the following expressions:

^b $\tau_{ij} = (a_{ij})$ and $G_{ij} = \exp(\alpha_{ij,NRTL} \tau_{ij})$ (Renon and Prausnitz, 1968)

^c $\tau_{ij} = a_{ij}$ (Abrams and Prausnitz, 1975)

Table 5.5. NRTL and UNIQUAC interaction parameters and root mean square deviations (RMSD) for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at (303.4, 308.1 and 309.0) K and 101.33 kPa.

Parameter	Temperature	
	$T = 303.4 \text{ K}$	
	NRTL ^b	UNIQUAC ^c
a_{12}	1.917	0.013
a_{21}	0.576	0.008
a_{13}	0.251	2.244
a_{31}	1.857	-0.530
a_{23}	-0.585	3.842
a_{32}	1.976	-1.281
$\alpha_{ij,NRTL}$	0.2	-
RMSD ^a	0.0005	0.0073
$T = 308.1 \text{ K}$		
	NRTL ^b	UNIQUAC ^c
a_{12}	2.518	0.186
a_{21}	0.110	0.123
a_{13}	5.896	-0.112
a_{31}	0.489	0.937
a_{23}	3.411	0.516
a_{32}	6.584	0.478
$\alpha_{ij,NRTL}$	0.2	-
RMSD ^a	0.0003	0.0013
$T = 309.0 \text{ K}$		
	NRTL ^b	UNIQUAC ^c
a_{12}	1.667	0.164
a_{21}	0.674	0.197
a_{13}	1.774	-0.044
a_{31}	0.933	1.083
a_{23}	-2.193	0.339
a_{32}	4.465	3.221
$\alpha_{ij,NRTL}$	0.2	-
RMSD ^a	0.0001	0.0002

$$^a \text{RMSD} = \left(\frac{\sum_1^N \sum_2^N \sum_3^N (x_i^{\alpha \text{exp}} - x_i^{\alpha \text{calc}})^2}{6N} \right)^{1/2}$$

Model parameters can be related to those described in the original works by the following expressions:

^b $\tau_{ij} = a_{ij}$ and $G_{ij} = \exp(\alpha_{ij,NRTL} \tau_{ij})$ (Renon and Prausnitz, 1968)

^c $\tau_{ij} = a_{ij}$ (Abrams and Prausnitz, 1975)

Table 5.6. Calculated plait points for ternary LLE systems using intermediate point method (Mangiapia et al., 2016).

T/K	x ₁	x ₂	x ₃
methanol (1) + n-hexane (2) + pentan-2-one (3)			
300.3	0.256	0.527	0.217
303.2	0.300	0.508	0.193
307.3	0.342	0.551	0.107
methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3)			
303.4	0.437	0.469	0.095
308.1	0.393	0.550	0.057
309.0	0.426	0.552	0.022

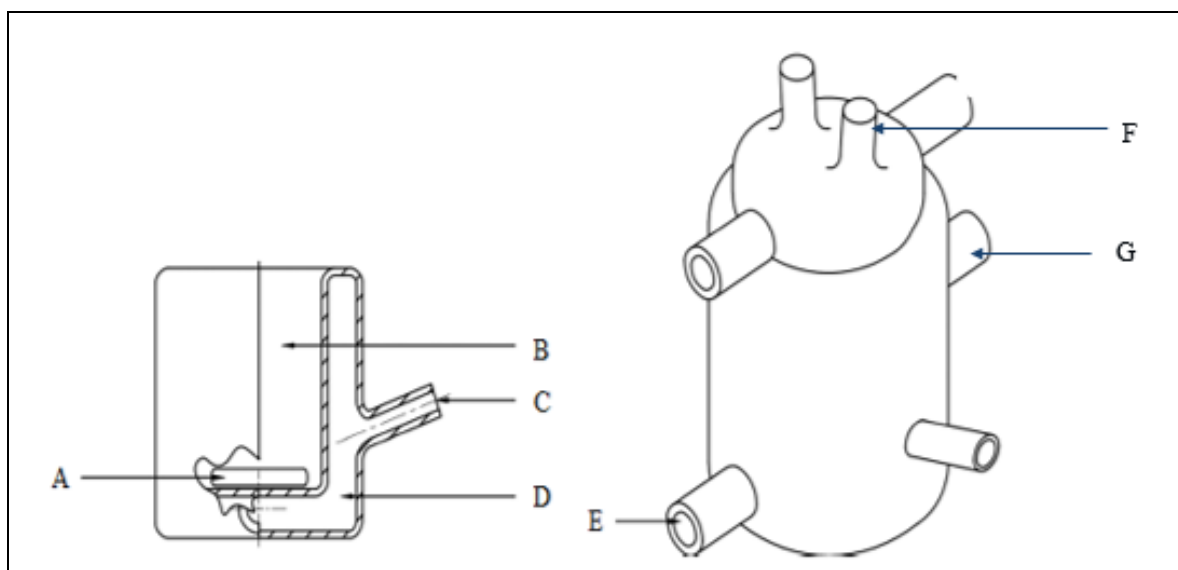


Figure 5.1. Schematic of LLE cell used (taken from Narasigadu et al. (2014)) (A) 14 mm stirrer bead; (B) Inner cell cavity; (C) Bottom sample point; (D) Cell wall cavity for heating fluid; (E) Cell heating fluid inlet; (F) Cell heating fluid outlet; (G) Top sample point.

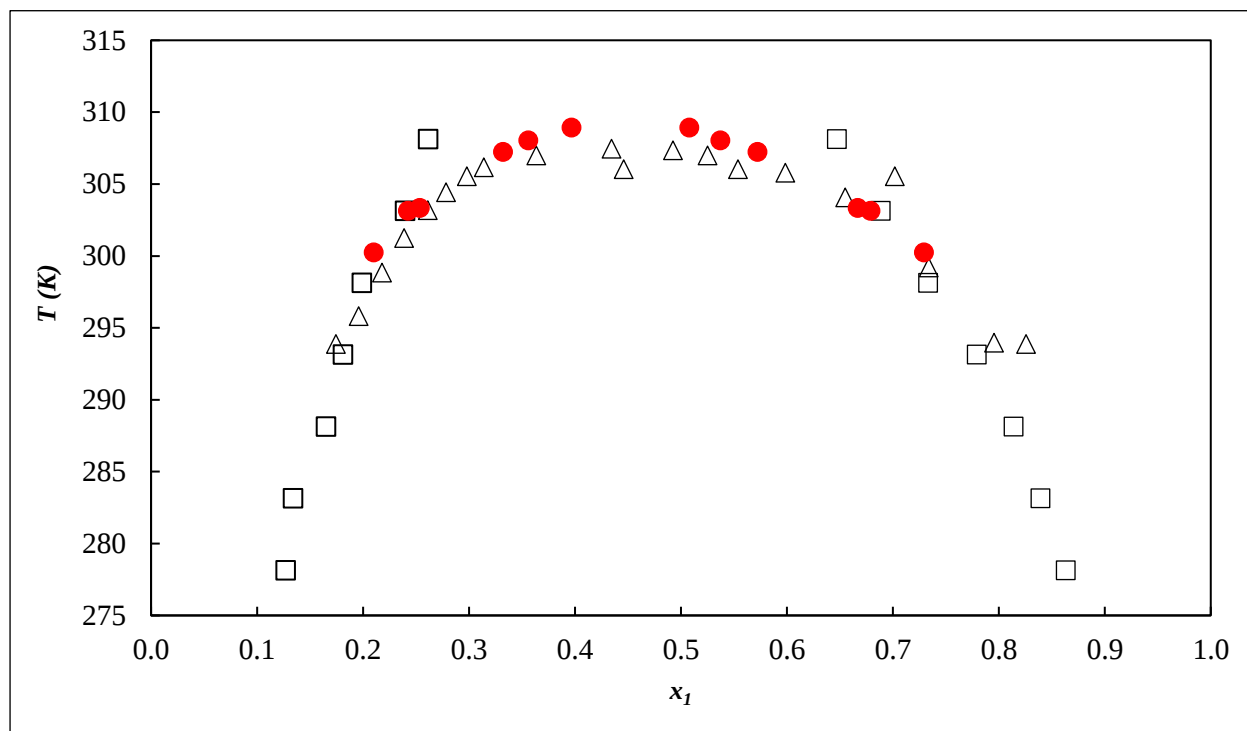


Figure 5.2. Comparison of binary LLE experimental data for the methanol (1) + n-hexane (2) system at 0.1 MPa (●) to literature data. △-(Blanco and Ortega, 1996), □-(Orge et al., 1997).

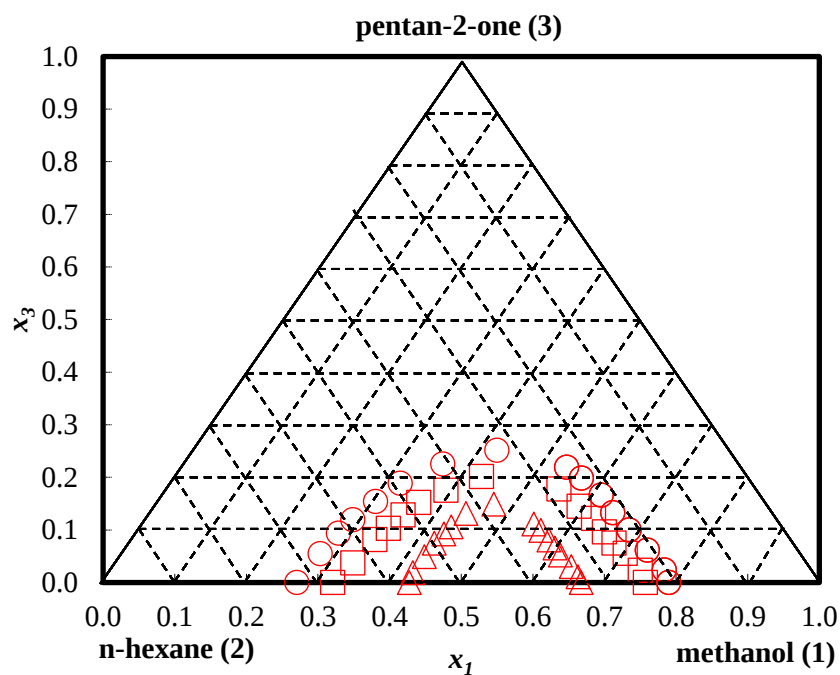


Figure 5.3. Experimental LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (○-300.3, ◻-303.2, Δ-307.3) K and 0.1 MPa.

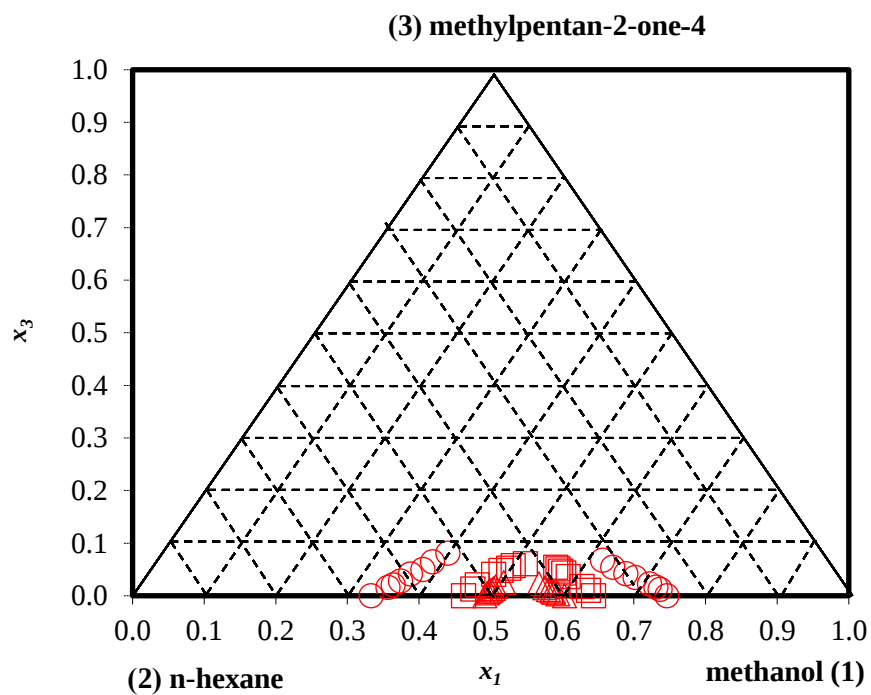


Figure 5.4. Experimental LLE data for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at ($\circ$ -303.4, $\square$ -308.1, $\triangle$ -309.0) K and 0.1 MPa.

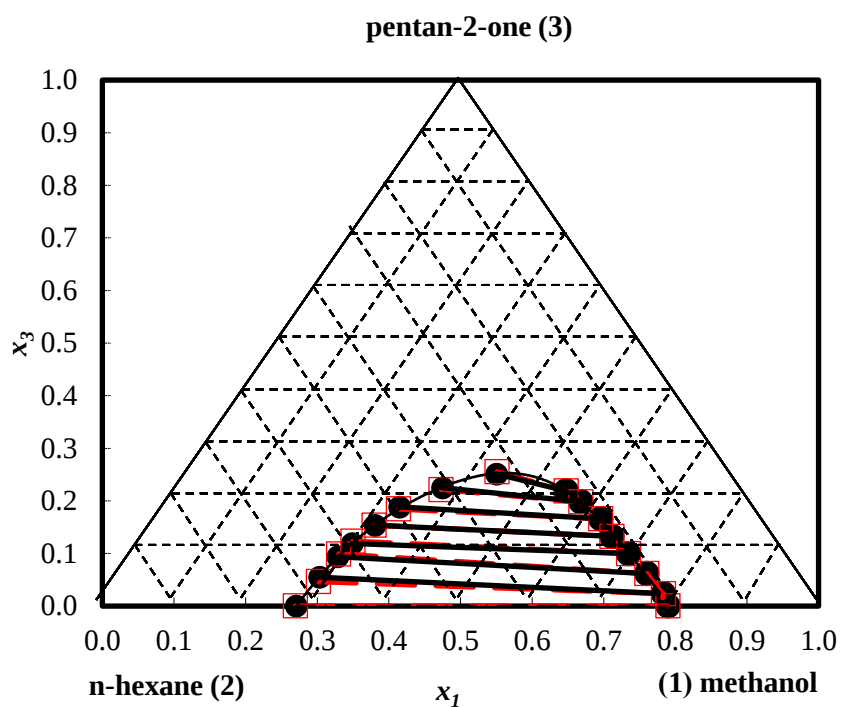


Figure 5.5. LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at 300.3 K and 0.1 MPa, LLE (experimental, tie-line) (●, —), correlated NRTL model (□, —).

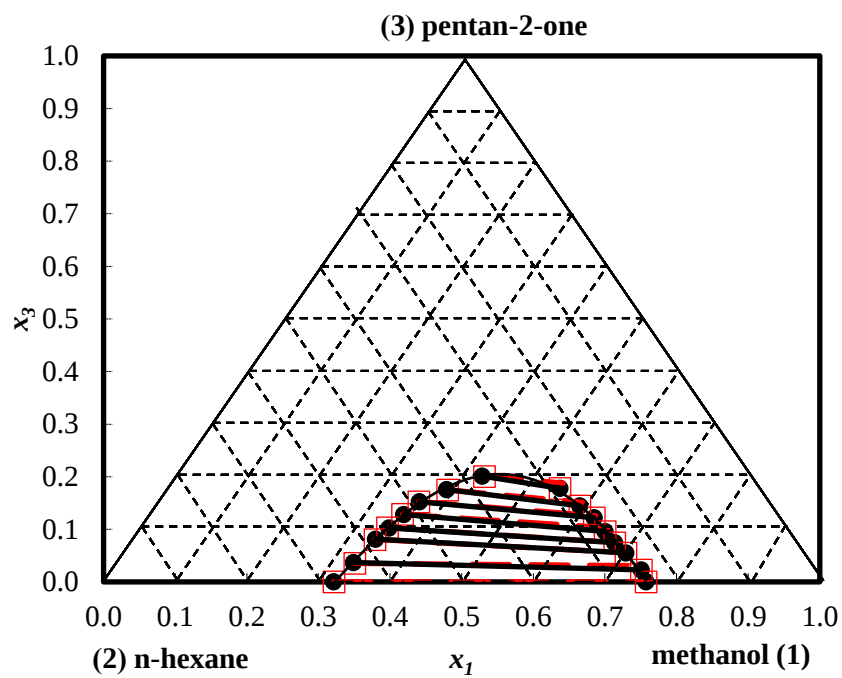


Figure 5.6. LLE data for the methanol (1) + n hexane (2) + pentan-2-one (3) system at 303.2 K and 0.1 MPa, LLE (experimental, tie-line) ($\bullet$, —), correlated NRTL model ($\square$, —).

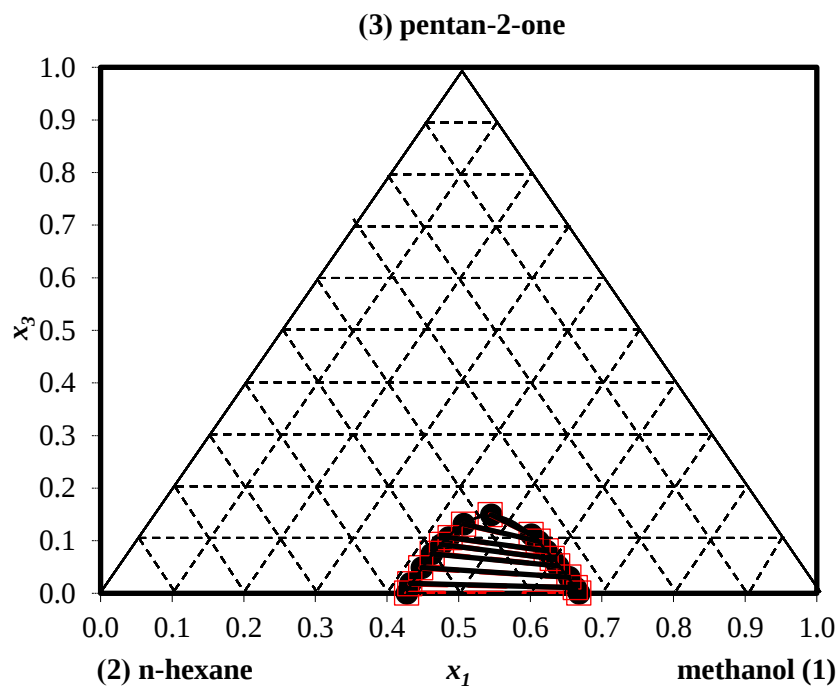


Figure 5.7. LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at at 307.3 K and 0.1 MPa, LLE (experimental, tie-line) (●, —), correlated NRTL model (□, —).

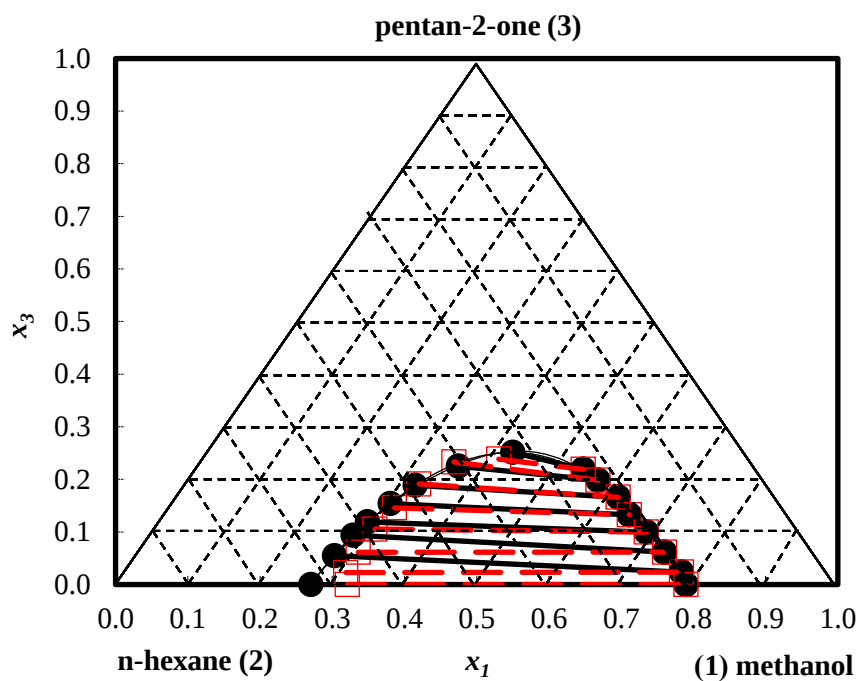


Figure 5.8. LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at 300.3 K and 0.1 MPa, LLE (experimental, tie-line) (•, —), correlated UNIQUAC model (□, —).

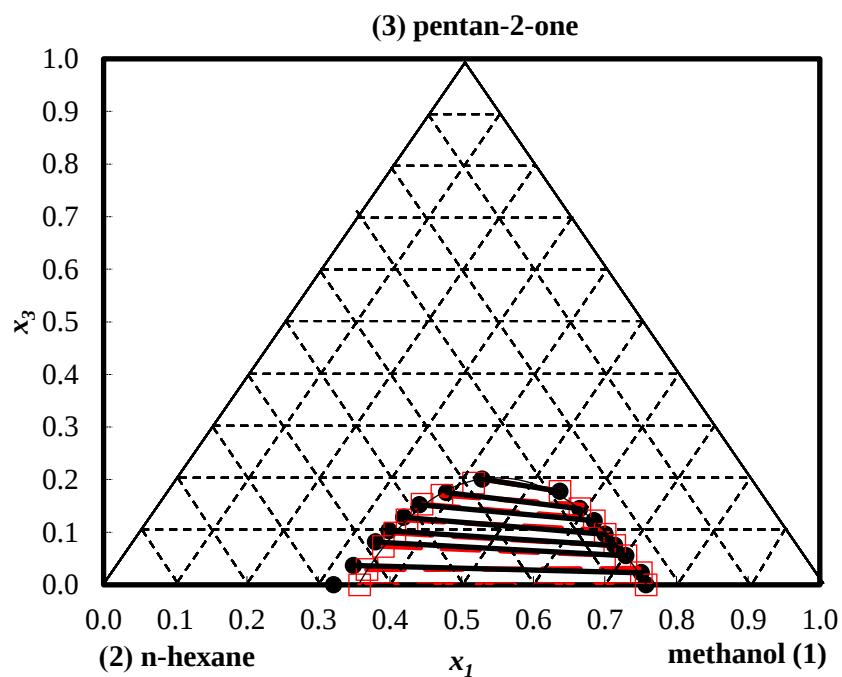


Figure 5.9. LLE data for the methanol (1) + n hexane (2) + pentan-2-one (3) system at 303.2 K and 0.1MPa, LLE (experimental, tie-line) (•, —), correlated UNIQUAC model (□, —).

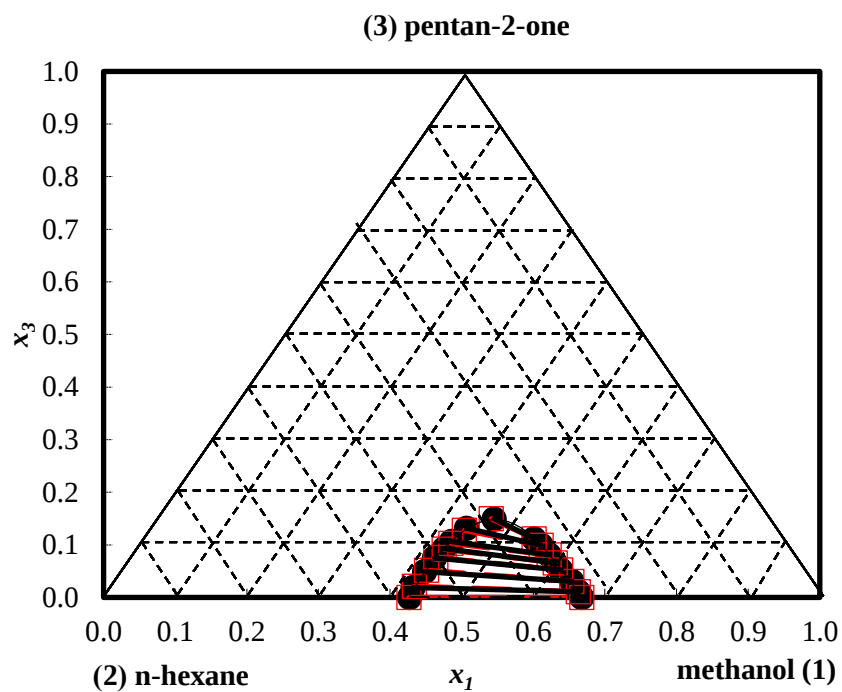


Figure 5.10. LLE data for the methanol (1) + n hexane (2) + pentan-2-one (3) system at 307.3 K and 0.1 MPa, LLE (experimental, tie-line) (•, —), correlated UNIQUAC model (□, —).

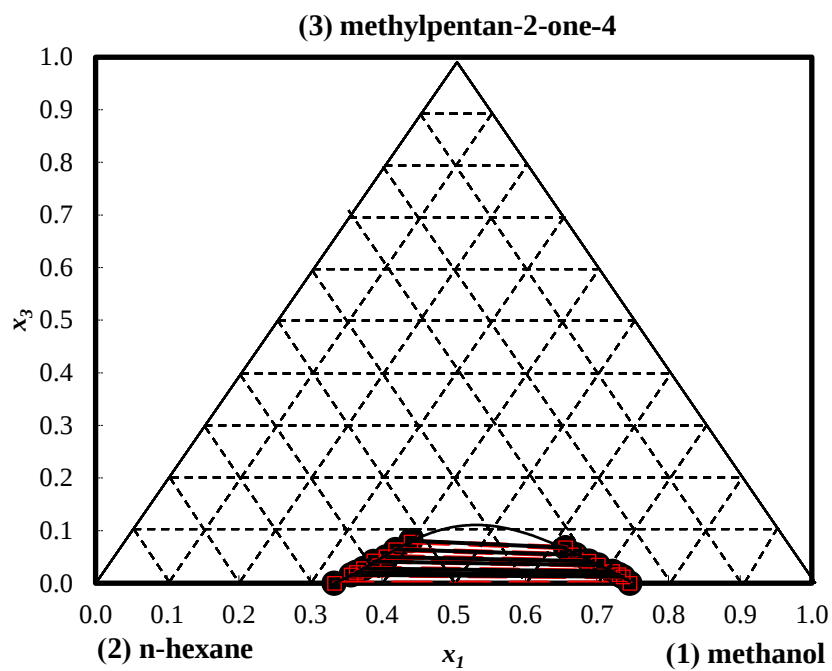


Figure 5.11. LLE data for the methanol (1) + n hexane (2) + 4-methylpentan-2-one (3) system at 303.4 K and 0.1MPa, LLE (experimental, tie-line) (•, —), correlated NRTL model (□, —).

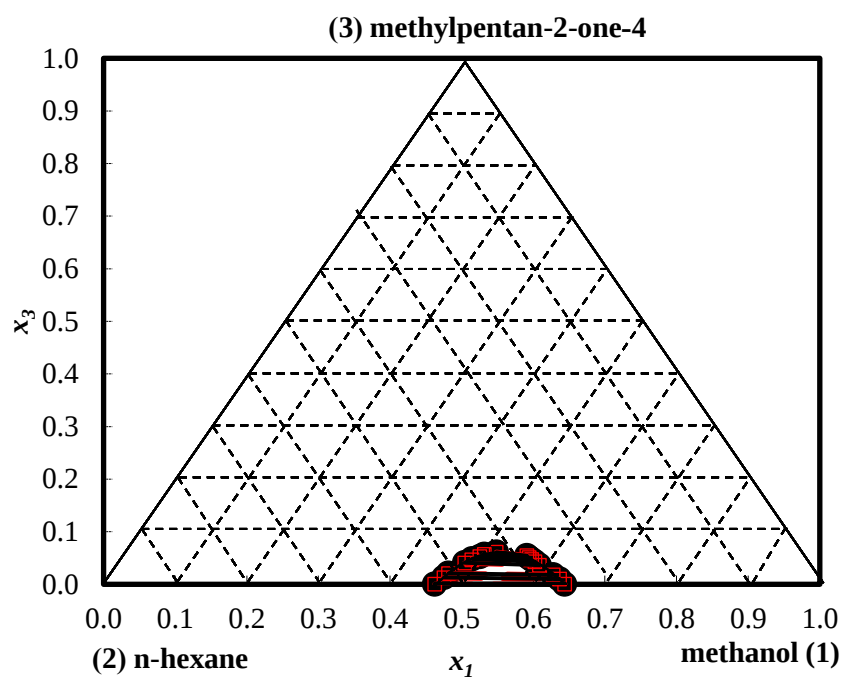


Figure 5.12. LLE data for the methanol (1) + n hexane (2) + 4-methylpentan-2-one (3) system at 308.1 K and 0.1MPa, LLE (experimental, tie-line) ($\bullet$, —), correlated NRTL model ($\square$, —).

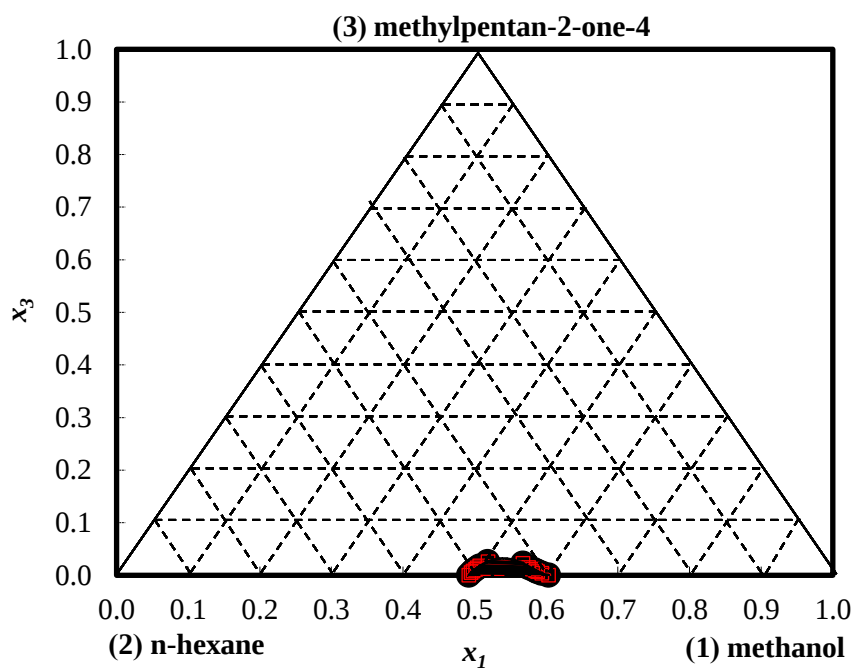


Figure 5.13. LLE data for the methanol (1) + n hexane (2) + 4-methylpentan-2-one (3) system at 309.0 K and 0.1MPa, LLE (experimental, tie-line) ($\bullet$, —), correlated NRTL model ($\square$, —).

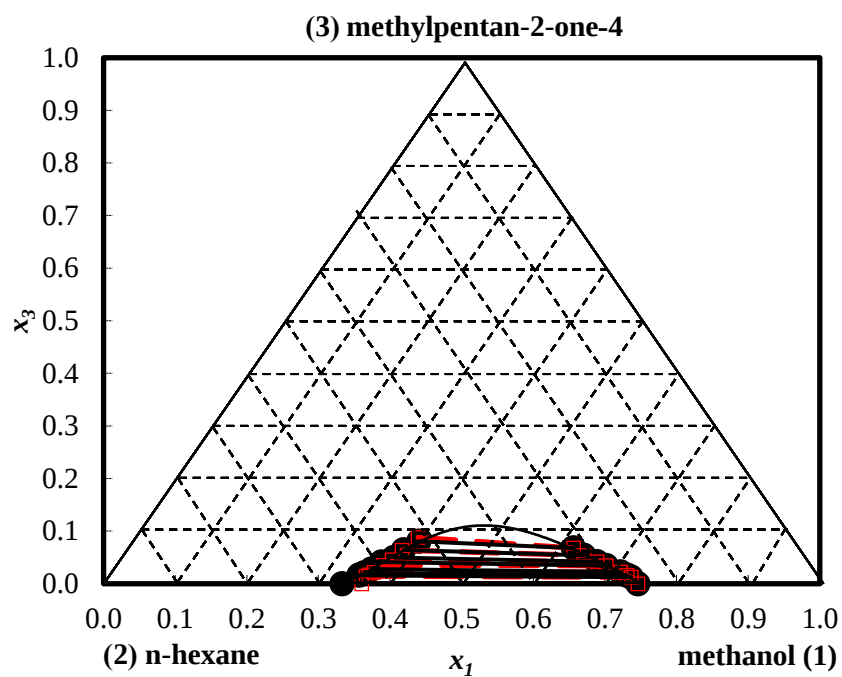


Figure 5.14. LLE data for the methanol (1) + n hexane (2) + 4-methylpentan-2-one (3) system at 303.4 K and 0.1MPa, LLE (experimental, tie-line) (●, —), correlated UNIQUAC model (□, —).

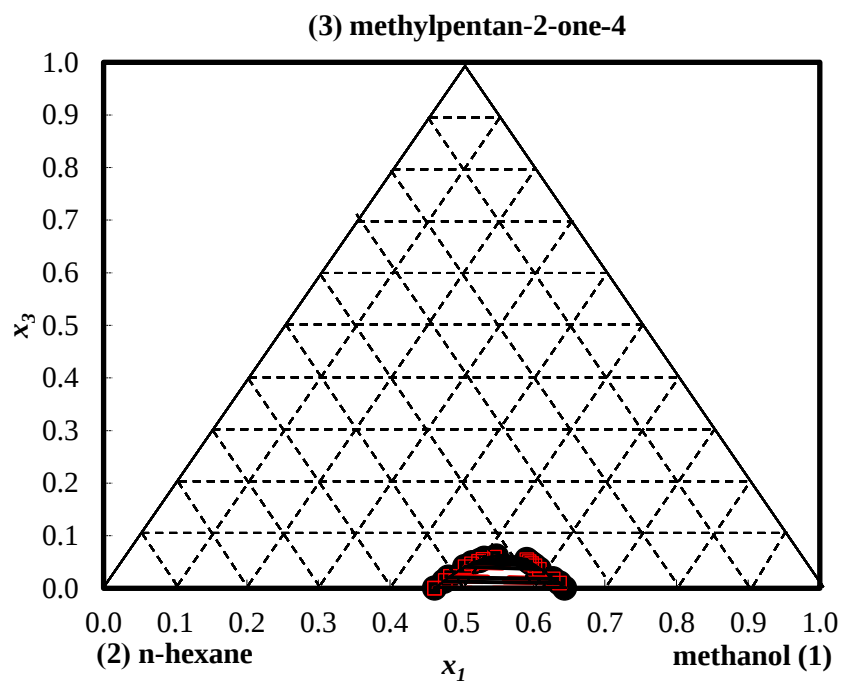


Figure 5.15. LLE data for the methanol (1) + n hexane (2) + 4-methylpentan-2-one (3) system at 308.1 K and 0.1MPa, LLE (experimental, tie-line) (●, —), correlated UNIQUAC model (□, —).

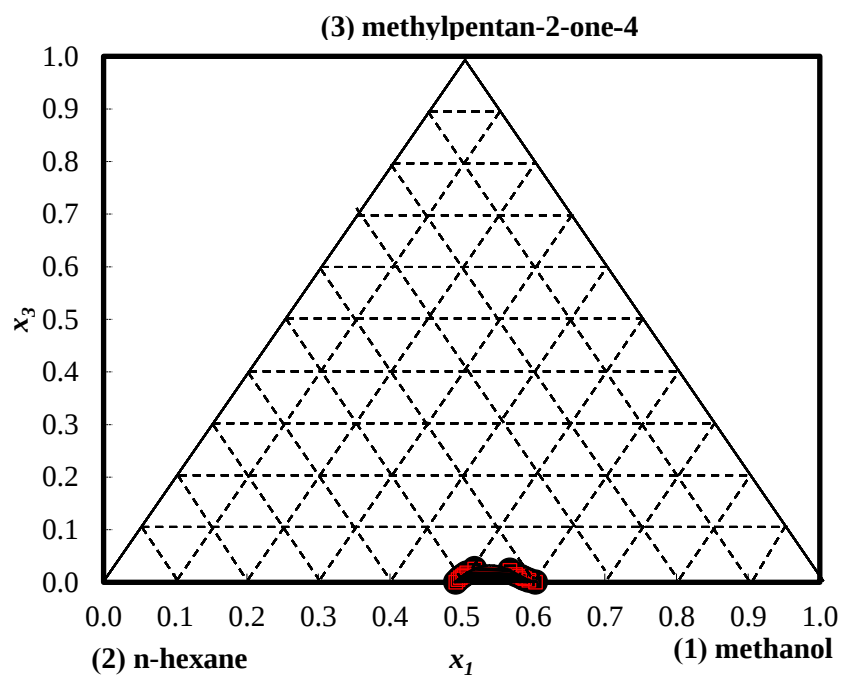


Figure 5.16. LLE data for the methanol (1) + n hexane (2) + 4-methylpentan-2-one (3) system at 309.0 K and 0.1MPa, LLE (experimental, tie-line) (●, —), correlated UNIQUAC model (□, —).

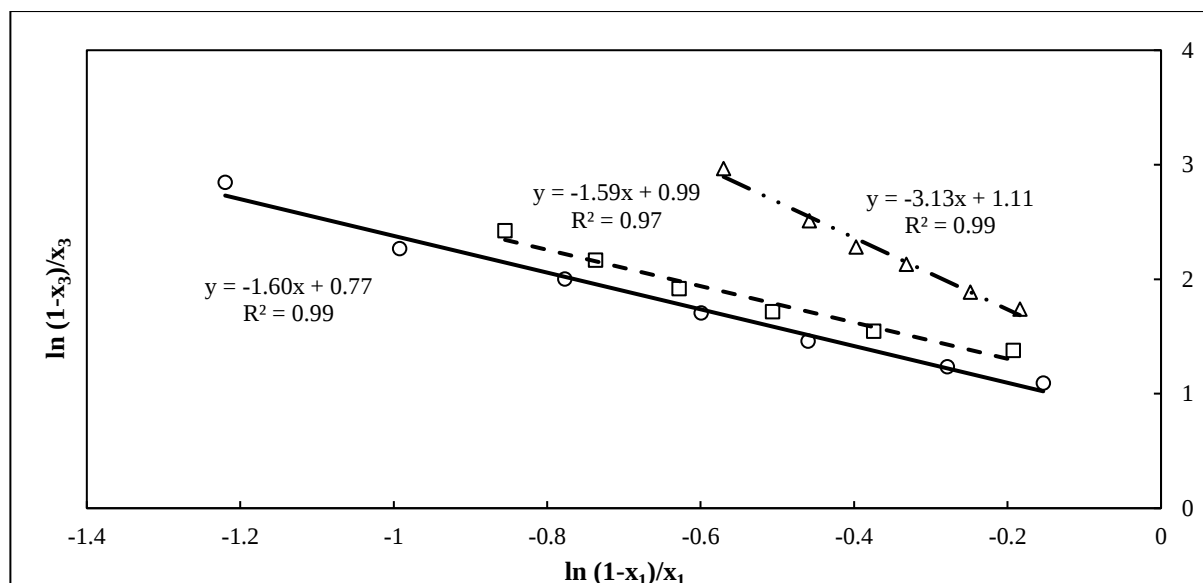


Figure 5.17. Linearity test from the Othmer-Tobias plot for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (Othmer-Tobias equation, linear correlation) (($\circ$, —)-300.3, ($\square$, - - -)-303.2, (Δ , — · —)-307.3) K.

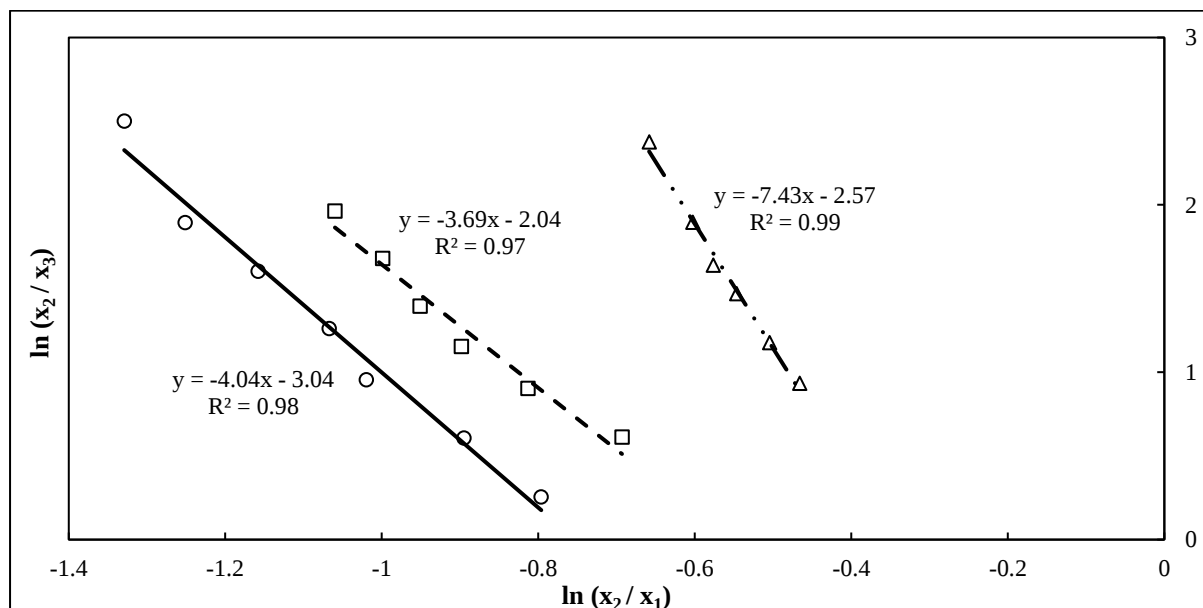


Figure 5.18. Linearity test from the Hand plot for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (Hand equation, linear correlation) (($\circ$, —)-300.3, ($\square$, - - -)-303.2, (Δ , — · —)-307.3) K.

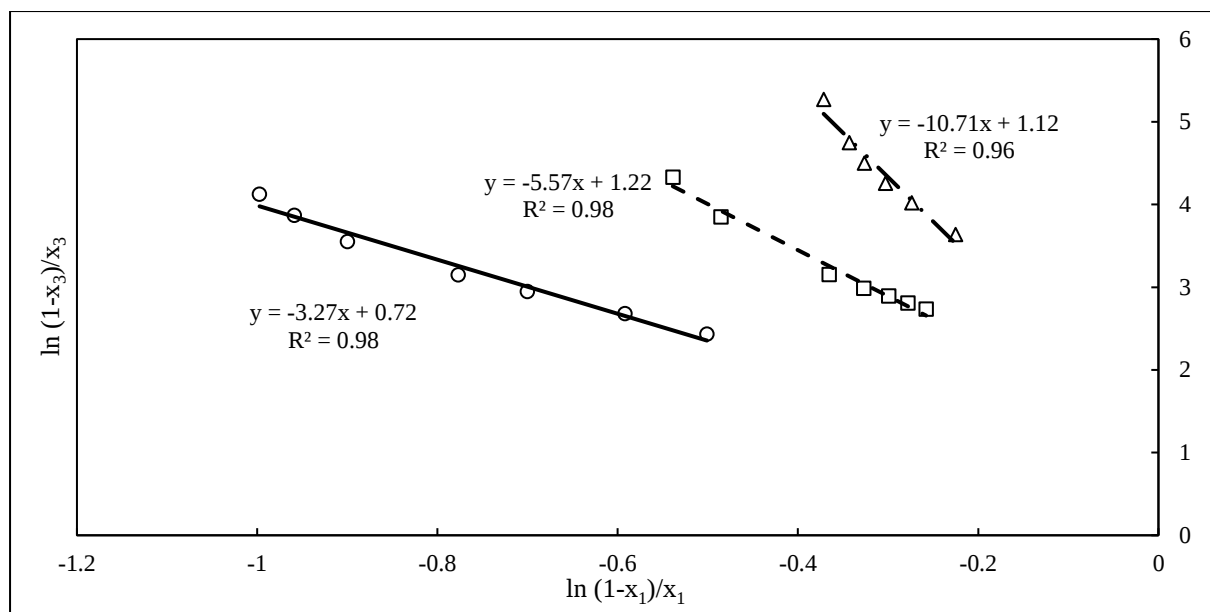


Figure 5.19. Linearity test from the Othmer-Tobias plot for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at (Othmer-Tobias equation, linear correlation) (($\circ$, —)-303.4, ($\square$, - - -)-308.1, (Δ , —·—)-309.0) K.

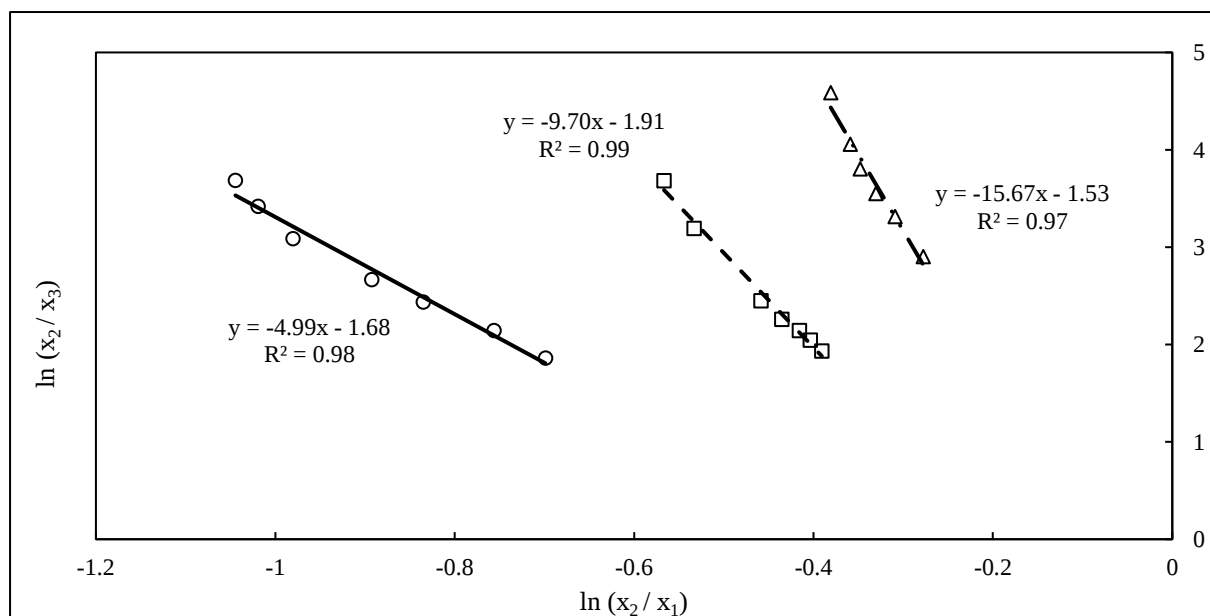


Figure 5.20. Linearity test from the Hand plot for the methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) system at (Hand equation, linear correlation) (($\circ$, —)-303.4, ($\square$, - - -)-308.1, (Δ , —·—)-309.0) K.

CHAPTER SIX

Culminating discussion

From the binary vapour-liquid equilibrium (VLE) measurements of n-hexane + pentan-2-one/4-methylpentan-2-one and binary, ternary and quaternary liquid-liquid equilibrium (LLE) data measurements of methanol + n-hexane + pentan-2-one/4-methylpentan-2-one, the separation potential and blending limits of the components in these mixtures were studied. n-Hexane was used as a representative component for a light gasoline cut. This experimental data was then modelled on Aspen Plus software and residue curves, and distillation and extraction boundaries were identified. The blending and separation limits were identified by phase boundaries, and critical points such as azeotropes and plait points. This chapter presents a concise summary of the details of the chemicals used and uncertainty of measurements, VLE and LLE experimental and model results as well as the discussion of separation potential and blending limits of the systems studied.

6.1. Chemicals and uncertainty

All chemicals used in the experimental work were purchased from Sigma-Aldrich with the supplier stated mass purities exceeding 0.99 mass fraction. The hydrophilic chemicals (ketones and methanol) were dried by molecular sieve and Karl Fischer titrations were performed to determine the water content by employing an MKS 500 device. The water content was found to be below 0.0005 mass fraction. The pure samples of all the components used in this study were then analysed using a gas chromatograph to confirm the purity. The GC analysis for the pure components resulted in relative GC peak areas of >0.99 fraction. Refractive indices of the pure chemicals were determined at $T = 293.15\text{ K}$ by using an ATAGO RX-7000 α refractometer (sodium D-line = 589 nm) with a supplier uncertainty of 0.0001 and densities were measured at $T = 298.15\text{ K}$ using an Anton Paar DSA 5000M apparatus with a supplier-stated accuracy of $0.007\text{ kg}\cdot\text{m}^{-3}$. The properties of the chemicals from the VLE and LLE studies are reported in Chapters 4 and 5.

The GC area ratio method of Raal and Mühlbauer (1998) was used to calibrate the thermal conductivity detector of the gas chromatograph. The standard mixtures for the calibration were prepared gravimetrically with acetone being used as an internal standard for the immiscible

mixtures. A Mettler-Toledo mass balance (model AB204-S) with an uncertainty of 0.0001g was used. The standard combined uncertainty in composition was calculated to be 0.005 mole fraction for both VLE and the LLE measurements. For the VLE measurements, pressure was controlled by using an ABB F080 pressure controller. The desired setpoint pressure was maintained by subjecting the still to vacuum or venting to the atmosphere. A WIKA P-10 transducer, with a supplier uncertainty of 0.05kPa, was used to measure the equilibrium pressure. This WIKA P-10 transducer was calibrated using a WIKA CPC 3000 pressure controller as a standard. The standard combined uncertainty in pressure was calculated to be 0.1 kPa. A type-A Pt-100 temperature probe was used to measure the equilibrium temperature within the equilibrium chamber. This probe was calibrated using a WIKA CTB 9100 temperature standard with a reported uncertainty of 0.05 K. The standard combined uncertainty in temperature for VLE measurements was calculated to be 0.1 K.

For the LLE measurements, the equilibrium temperature was determined by using a Pt-100 class-A temperature sensor and was calibrated using a WIKA CTB 9100 temperature standard. The standard combined uncertainty in temperature was calculated to be 0.1 K. All calibration results for VLE and LLE measurements are presented in Appendix A. For all uncertainty calculations, procedures outlined by NIST JCGM (ISO, 2008) were followed and the uncertainty calculations explained in Appendix B. The combined uncertainties were calculated by type A and type B propagation of errors and took into account the supplier uncertainty, uncertainty from calibration, uncertainty from repeatability and the uncertainty introduced by chemical impurity in the relevant calculations.

6.2. VLE measurements and modelling

6.2.1. Binary VLE test system

To confirm the equipment and procedure used in this work for the VLE measurements, vapour pressure measurements were conducted for several pure components over the temperature range considered. The experimental values showed a close correlation to calculated values using the Antoine prediction. A binary isothermal VLE test measurement for the system of propan-1-ol + n-heptane at approximately 333 K was also conducted and compared to literature. The vapour pressure results are presented in Chapter 4 and binary test system results are presented in Appendix C in Table C-1 and Figures C-1-C-2. The data from this work is in good agreement with the literature sources at similar operating conditions and is within the

expanded combined uncertainties of all studies considering temperature, pressure and composition. Maximum deviations in pressure between relative studies did not exceed 1 kPa and are attributed to experimental uncertainties in temperature, pressure and composition, chemical purities, and the sophistication of equipment/techniques between studies.

6.2.2. Novel binary VLE data

Novel isothermal vapour–liquid equilibrium (VLE) data were measured for the hexane + pentan-2-one/4-methylpentan-2-one systems, to characterize the separation limits for distillation, as discussed in Chapter 4. Measurements were undertaken at approximately 313.3, 323.3, and 333.5 K for the n-hexane (1) + pentan-2-one (2) system and 313.3, 323.3, and 333.6 K for the n-hexane (1) + 4-methylpentan-2-one (2) system. The behaviour of the systems measured was highly non-ideal and exhibited a strong positive deviation from Raoult’s law. Azeotropic behaviour was observed for the n-hexane (1) + pentan-2-one (2) system at all measured temperatures. The azeotropic compositions for this system are outlined in Chapter 4. For the n-hexane (1) + 4-methylpentan-2-one (2) system, azeotropic behaviour was not observed from the experimental results. The VLE x-y plots are presented in Appendix D-1-D-6.

The γ - Φ approach was used to correlate the VLE data using the NRTL-HOC and UNIQUAC-HOC thermodynamic property methods. The NRTL and UNIQUAC models accounted for liquid phase non-ideality and the virial equation of state with the Hayden and O’Connell correlation accounted for the vapour phase non-ideality. The root mean square deviation (RMSD) values were between 0.025 and 0.048 kPa and was within the experimental uncertainty in pressure. The model parameters, RMSD values and absolute average deviations (AAD) in vapour composition for both systems are presented in Chapter 4. From the RMSD values in pressure and AAD in vapour composition, the NRTL-HOC and UNIQUAC-HOC model correlations are very similar, but the model deviations show that the UNIQUAC-HOC model performs slightly better than the NRTL-HOC model.

The data was also modelled by use of the Peng–Robinson (PR) (Peng and Robinson, 1976) equation of state and the perturbed-chain statistical associating fluid theory (PC-SAFT) (Gross and Sadowski, 2001) equation of state by the ϕ - ϕ approach as a comparison to the γ - Φ approach. It was found that the activity coefficient models with the virial equation of state

provided a superior representation of the experimental data. These results along with the RMSDs in pressure and AAD in vapour composition are presented in Chapter 4.

The area test of Redlich and Kister (1948) and point test of Christiansen & Fredenslund (1975) were applied to the VLE data to assess the consistency of the experimental data. The results confirm that the data are thermodynamically consistent according to these tests and are presented in Chapter 4 with plots shown in shown in Appendix E, Figures E-1-E-10. The measured data also passed the infinite dilution test of Kojima et al. (1990) using the standard tolerances which is shown in Appendix E.

6.3. Liquid-liquid equilibrium measurements and modelling

6.3.1. Binary LLE test system

Liquid-liquid equilibrium (LLE) data were measured where the ketones were considered as an LLE solvent for the separation of methanol-n-hexane mixtures. To confirm the procedure used in this work the binary system of methanol (1) + n-hexane (2) at approximately (300, 303, 307, 308, 309) K and 0.1 MPa were measured and compared to literature shown in Chapter 5. The data measured show a good correlation within experimental uncertainty in temperature and composition to the measurements by Blanco and Ortega (1996), for the majority of the composition range. The upper critical solution temperature for the mixture is within the limits of the two available literature sources. This is shown in Appendix C, Table C-2 and Figure C-3. Standard uncertainties are reported by Blanco and Ortega (1996) as 0.001 for the liquid phase composition and 0.01 K in temperature, while the standard uncertainties reported in this work are 0.005 mole fraction and 0.1 K. Deviations between relative studies do not exceed 0.2 K and are attributed to experimental uncertainties in temperature and composition, chemical purities and the sophistication of equipment/techniques between studies.

6.3.2. Novel ternary LLE data

Novel data for the ternary systems of methanol (1) + n-hexane (2) + pentan-2-one (3) at approximately (300.3, 303.2, 307.3) K, and methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) at approximately (303.4, 308.1, 309.0) K, and 0.1 MPa were measured to characterize the liquid-liquid separation and blending limits for the mixtures and for process design. The non-random two liquid (NRTL) (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) activity coefficient models were used to correlate the experimental tie-lines

using non-linear least-squares regression. The correlated model parameters, experimental and modelled LLE data, and corresponding ternary diagrams are presented in Chapter 5. The RMSD was calculated to determine the performance of each model. There was a satisfactory correlation of the experimental data for both the NRTL and UNIQUAC models which were within the experimental uncertainty. From the calculated RMSD values in composition, it was seen that the NRTL model provides a better representation of the experimental data. The RMSD results are presented in Chapter 5. These values are between 0.0001 and 0.002 for the NRTL model and between 0.0002 and 0.015 for the UNIQUAC model.

The relative reliability of the individual tie-lines can be evaluated by linearity testing of the experimental LLE data. This was done by applying the Othmer & Tobias (1942) and Hand (Brandani et al., 1985) equations to the measured tie-line data. According to Carniti et al. (1978), the linearity of these correlations can be used to evaluate the reliability of a particular tie-line for a system in comparison to the others but cannot be used to confirm the “consistency” of LLE data. The Othmer-Tobias and Hand plots for both systems show a reasonable linear behaviour of $R^2 \geq 0.96$ which indicates that the measured tie-line data follow the expected trend given by the Othmer-Tobias and Hand correlations. However, due to the significant gradient change in the tie-lines from the respective horizontal binary tie-line for the methanol (1) + n-hexane (2) + pentan-2-one (3) system at (300.3 and $x_1^I = 0.772$, $x_1^{II} = 0.276$) and at (303.2 K and $x_1^I = 0.739$ and $x_1^{II} = 0.331$), the tie lines did not conform to a linear trend with the other tie-lines according to the Othmer-Tobias and Hand correlations

6.3.3. Quaternary LLE measurements

The experimental quaternary LLE data for the methanol (1) + n-hexane (2) + pentan-2-one (3) + 4-methylpentan-2-one (4) system was measured at (303.2, 308.2 and 313.2) K. The results are presented in Table 6.1 and Figure 6.1. and demonstrates clearly the form and arrangement of the binodal surface separating homogeneous and heterogeneous areas of compositions in the composition tetrahedron.

Table 6.1. Experimental liquid-liquid equilibrium data for the methanol (1) + n-hexane (2) + pentan-2-one (3) + 4-methylpentan-2-one (4) system at (303.2, 308.2 and 313.2) K and 0.1 MPa.^a

Lower phase (I)				Upper phase (II)					
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4	β^1	β^2
$T = 303.2$ K									
0.563	0.301	0.109	0.027	0.405	0.449	0.117	0.029	1.465	1.403
0.579	0.297	0.099	0.025	0.393	0.474	0.107	0.027	1.552	1.479
0.600	0.290	0.088	0.022	0.390	0.490	0.096	0.024	1.656	1.579
0.626	0.283	0.073	0.018	0.380	0.522	0.078	0.020	1.739	1.659
0.656	0.270	0.059	0.015	0.371	0.548	0.065	0.016	1.903	1.819
0.681	0.263	0.045	0.011	0.365	0.564	0.056	0.014	2.301	2.215
0.708	0.253	0.031	0.008	0.359	0.583	0.047	0.012	2.990	2.910
0.719	0.250	0.025	0.006	0.349	0.613	0.030	0.008	2.504	2.439
$T = 308.2$ K									
0.521	0.369	0.088	0.022	0.473	0.408	0.095	0.024	1.196	1.183
0.543	0.363	0.075	0.019	0.457	0.437	0.085	0.021	1.335	1.313
0.561	0.356	0.066	0.016	0.452	0.452	0.077	0.019	1.430	1.406
0.577	0.352	0.056	0.014	0.449	0.469	0.066	0.016	1.487	1.459
0.598	0.348	0.043	0.011	0.446	0.487	0.054	0.013	1.674	1.644
0.609	0.349	0.034	0.008	0.443	0.500	0.046	0.011	1.858	1.832
0.617	0.350	0.026	0.007	0.440	0.514	0.037	0.009	1.957	1.942
0.637	0.347	0.013	0.003	0.438	0.536	0.021	0.005	2.422	2.394
$T = 313.2$ K									
0.501	0.388	0.089	0.022	0.479	0.408	0.091	0.023	1.068	1.061
0.517	0.381	0.082	0.020	0.464	0.431	0.084	0.021	1.141	1.129
0.540	0.371	0.071	0.018	0.460	0.445	0.076	0.019	1.243	1.224
0.566	0.373	0.049	0.012	0.455	0.474	0.056	0.014	1.435	1.413
0.575	0.375	0.041	0.010	0.455	0.487	0.047	0.012	1.442	1.430
0.585	0.375	0.032	0.008	0.452	0.500	0.038	0.010	1.556	1.538
0.593	0.376	0.025	0.006	0.449	0.514	0.030	0.007	1.572	1.552
0.605	0.374	0.017	0.004	0.449	0.524	0.022	0.005	1.693	1.676

^a Standard combined uncertainties are $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(x_i) = 0.005$

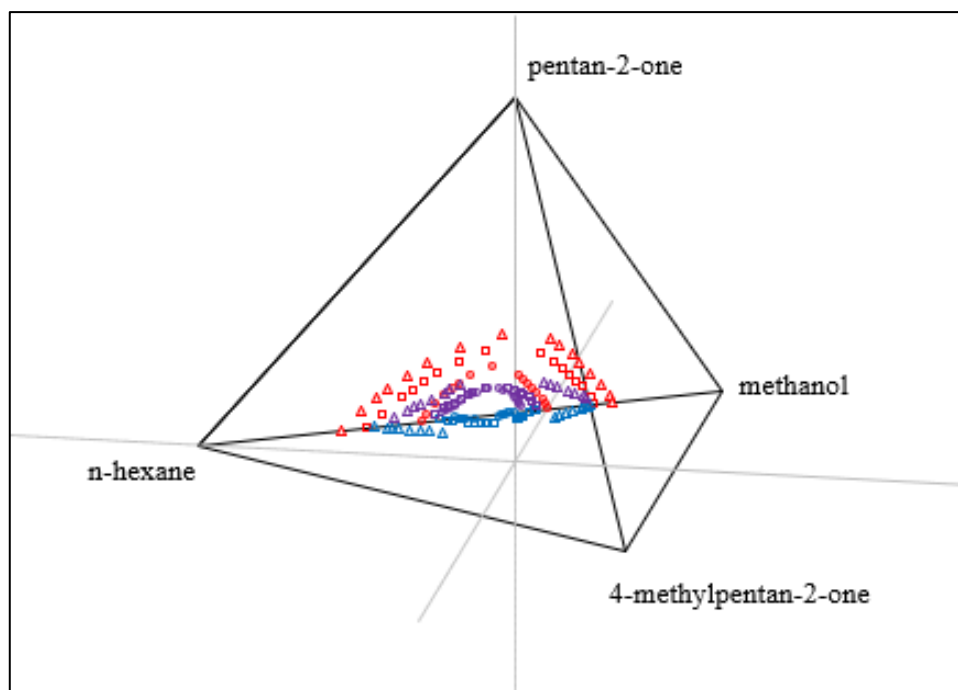


Figure 6.1 Schematic representation of liquid + liquid equilibrium data of the methanol (1) + n-hexane (2) + pentan-2-one (3) + 4-methylpentan-2-one (4) quaternary system at (Δ - 303.2, $\square$ - 308.2, $\circ$ - 313.2) K, methanol (1) + n-hexane (2) + pentan-2-one (3) ternary system at (Δ -300.3, $\square$ -303.2, $\circ$ -307.3) K and methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) ternary systems at (Δ -303.4, $\square$ -308.1, $\circ$ -309.0) K and 0.1 MPa.

6.4. Separation and blending limits

The phase envelope with azeotropes in the relevant binary VLE systems represent the separation limits by conventional distillation. From the modelled VLE data, the relative volatility for the n-hexane + 4-methylpentan-2-one system was found to be higher than in the n-hexane + pentan-2-one system. Therefore, it is likely that the separation of this mixture by distillation would be easier if some alternate technique was used to overcome the azeotrope in the n-hexane + pentan-2-one system, such as pervaporation. This is also a significant consideration for solvent benchmarking in extraction applications for example, where solvent recoveries of pentanones/hexanones from alkane mixtures would be considered.

In the ternary LLE systems, the measured LLE binodal curve represents the boundary regions of conventional distillation for a single liquid phase. It also represents the blending limit of a mixture. The blending regions are the compositions that can be mixed for a homogenous liquid mixture and are represented by the area outside the binodal curve and the metastable region in the ternary diagrams. Both systems exhibit type I ternary LLE behaviour at all temperatures which suggests that the solutes and solvent (ketone + n-hexane/methanol) are completely miscible in the temperature range considered. It was found that 4-methylpentan-2-one is able to homogenize the methanol - n-hexane mixture to a greater extent than pentan-2-one, which is a useful benchmark for blending applications.

The principles of employing phase diagrams for the design of unit operations in liquid-liquid extraction or extractive distillation is analogous to that which is employed in conventional distillation (Coquelet and Ramjugernath, 2012). Some examples include the use of T-x-y diagrams to determine the number of theoretical stages for separation, residue curves for distillation boundaries or ternary LLE diagrams for miscibility regions. Figure 6.2 and 6.3 show the residue curve map for the methanol (1) + n-hexane (2) + pentan-2-one (3) and methanol (1) + n-hexane (2) + 4-methylpentan-2-one (3) systems respectively at atmospheric pressure. The ketone solvents create an immiscibility region that encompasses the binary methanol-n-hexane heterogenous azeotrope (at approximately 0.5 mole fraction at 0.1 MPa). The data measured in this work shows that these ketone solvents can potentially be used to effectively separate the methanol-n-hexane azeotrope by a heterogenous distillation operation.

The residue curve map technique is considered to be a powerful tool for the flowsheet development and preliminary design of conventional multicomponent separation processes (Shen et al., 2016). The residue curve represents the change in the remaining liquid composition over time in a single-stage batch distillation process (Zuo et al., 2016). Therefore, residue curve diagrams are constructed to analyse the feasibility of the distillation process. The family of all residue curves that originate at one composition and terminate at another composition defines a distillation region. By combining the ternary diagrams with the residue curves as shown in Figures 6.2 and 6.3, the distillation and extraction process can be used together to achieve separation of the ternary systems via a heterogenous azeotropic distillation. In Figure 6.2 and 6.3, four fixed points are found on the ternary phase diagram, that is, a heterogeneous azeotropic point and three vertices. The nodes represent the points where the residue curves either start or end. A minimum heterogeneous azeotrope exists in the methanol + n-hexane +

pentan-2-one / 4-methylpentan-2-one ternary systems studied. Distillation regions are an important factor in assessing the feasibility of distillation processes since these boundaries determine whether it is possible to obtain the pure products from the process (Walpot, 2011). It can be seen in Figure 6.2 and 6.3 that all residue curves originate and terminate at the same two compositions on each diagram and therefore a single distillation region can be maintained. In both systems, the methanol-n-hexane azeotrope is the low-boiling node and the origin of all residue curves, and the ketone pure component node is the high-boiling node and terminus of all residue curves.

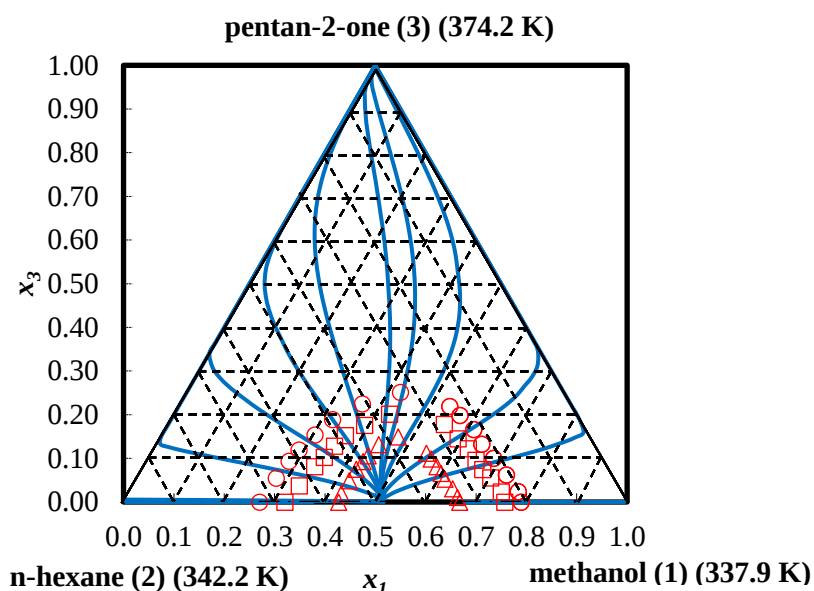


Figure 6.2 Residue curve diagram and experimental LLE data for the methanol(1) + n-hexane(2) + pentan-2-one(3) system at 101.3kPa, (○-300.3, ◻-303.2, Δ-307.3) K. Blue lines represent the residue curves.

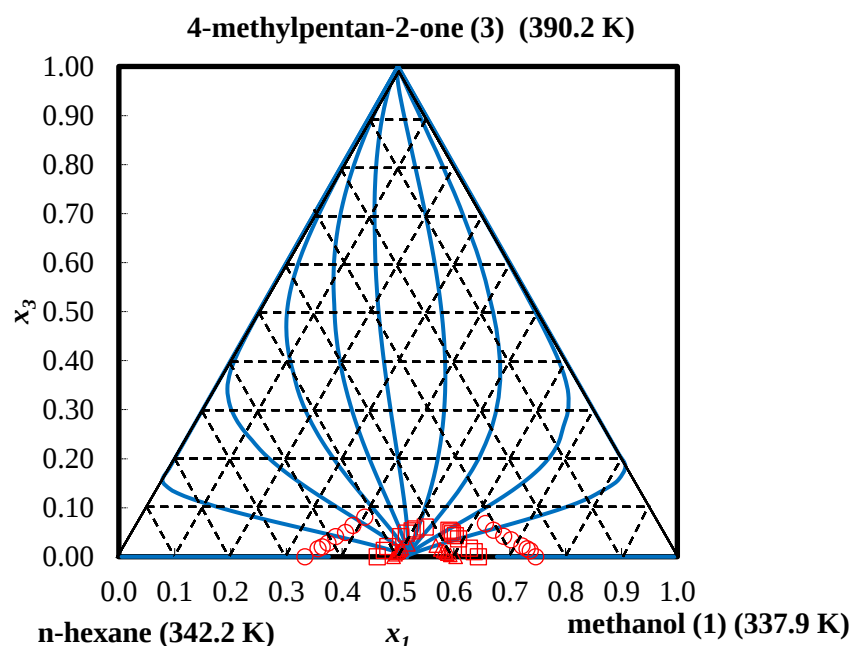


Figure 6.3 Residue curve diagram and experimental LLE data for the methanol(1) + n-hexane(2) + 4-methylpentan-2-one(3) system at 101.3kPa, (○-303.4, □-308.1, △-309.0) K. Blue lines represent the residue curves.

Solvent selection for liquid-liquid extraction is an important design consideration as it directly affects process efficiency. Relative selectivity (β) is a parameter used to measure the effectiveness of a solvent and a solvent would be regarded effective if β exceeds a value of 1. Consider for example, a liquid-liquid extraction process for the separation of methanol + pentan-2-one/4-methylpentan-2-one mixtures where n-hexane is proposed as an extraction solvent. The relative selectivity (β) of n-hexane was shown to be greater than unity, therefore n-hexane is an effective solvent in removing pentan-2-one/4-methylpentan-2-one from methanol mixtures. The relative selectivity (β) values of n-hexane are presented in Chapter 5. It was found that n-hexane is significantly more selective to pentan-2-one than 4-methylpentan-2-one. This was confirmed experimentally by performing quaternary LLE measurements for the n-hexane + methanol + pentan-2-one + 4-methylpentan-2-one systems as shown above.

In the case of the methanol (1) + n-hexane (2) + pentan-2-one (3) + 4-methylpentan-2-one (4) quaternary system, to characterize the suitability of n-hexane as an extraction solvent, the

selectivity, β^1 represents the relative selectivity of n-hexane to remove pentan-2-one from methylpentan-2-one + methanol mixtures and β^2 which represents the relative selectivity of n-hexane to remove 4-methylpentan-2-one from pentan-2-one + methanol mixtures. β^1 and β^2 are calculated as follows:

$$\beta^1 = \frac{x_3^{II}(x_1^I + x_4^I)}{x_3^I(x_1^{II} + x_4^I)} \quad (6.1)$$

$$\beta^2 = \frac{x_4^{II}(x_1^I + x_3^I)}{x_4^I(x_1^{II} + x_3^I)} \quad (6.2)$$

where the subscripts 1, 3 and 4 represent methanol, pentan-2-one and 4-methylpentan-2-one respectively, and *I* and *II* represent the n-hexane-dilute phase and the n-hexane-rich phase respectively.

The calculated selectivity from equation 6.1 and 6.2 takes into account the presence of methanol and both ketones. The calculated values are presented in Table 6.1. As with the ternary system, the selectivity is shown to be greater than unity therefore n-hexane is an effective extraction solvent. The β values calculated for the quaternary system are generally lower than those obtained for the ternary systems.

CHAPTER SEVEN

Conclusions

- Pure component vapour pressures, binary VLE, and binary LLE test measurements were performed to verify the experimental techniques used in this work. The isothermal VLE test system of propan-1-ol + n-heptane at approximately 333 K was in good agreement with literature and within experimental uncertainties, while the binary LLE system of methanol (1) + n-hexane (2) was measured at approximately (300, 303, 307, 308, 309) K and 0.1 MPa with deviations from literature not exceeding 0.2 K.
- Novel binary isothermal vapour–liquid equilibrium (VLE) data were successfully measured for the hexane + pentan-2-one/4-methylpentan-2-one systems at approximately $T = 313, 323, 333$ K and were found to be thermodynamically consistent, which confirmed the validity of the results obtained.
- The behaviour of the VLE systems measured was highly nonideal with azeotropic behaviour observed for the n-hexane (1) + pentan-2-one (2) system at compositions of 0.949, 0.969 and 0.970 at 313.3 K, 323.3 K and 333.5 K respectively. Azeotropic behaviour was not observed experimentally for the n-hexane (1) + 4-methylpentan-2-one (2) system.
- The NRTL model with virial EOS (HOC) and UNIQUAC model with virial EOS (HOC) correlated the data well and outperformed the modelling by the ϕ – ϕ approach using the Peng–Robinson and PC-SAFT equations of state. The values for the root-mean-square deviation (RMSD) for VLE pressures were found to be within the experimental uncertainty and were in the range of 0.025 to 0.048 kPa, confirming the accuracy of the modelling.
- For the VLE systems, the excess Gibbs energy and excess enthalpy were found to be positive for the entire composition range, and the predicted excess enthalpy correlated well with the literature where available, indicating coherence with literature.
- From the modelled VLE data, the relative volatility for the n-hexane + 4-methylpentan-2-one system was in the range of 1.06 and 18.3 and for the n-hexane-pentan-2-one

system it was between 0.90 to 11.50. Higher values for the n-hexane + 4-methylpentan-2-one system suggest that it is likely that the separation of this mixture by distillation would be easier if some alternate technique, such as pervaporation, was used to overcome the azeotrope in the n-hexane + pentan-2-one system.

- The methanol-n-hexane and methanol-n-hexane-ketone LLE systems studied were found to exhibit type I ternary LLE behaviour indicating that solutes and solvent (ketone + n-hexane/methanol) are completely miscible in the temperature range considered. The binary methanol-n-hexane heterogenous azeotrope is at approximately $x_1 = 0.5$ at 0.1 MPa.
- The NRTL and UNIQUAC thermodynamic models provided an acceptable correlation to the experimental data with the root mean square deviations (RMSD) within the experimental uncertainty of maximum 0.002 and to 0.015 for the NRTL and UNIQUAC models respectively. The methanol + n-hexane + pentan-2-one system gave the highest errors.
- The Othmer-Tobias and Hand plots for both systems show a reasonable linear behaviour of $R^2 \geq 0.96$ which indicates that the measured tie-line data follow the expected trend given by the Othmer-Tobias and Hand correlations.
- From the ternary LLE data, the binodal curves have been determined and represent the boundary regions of conventional distillation for a single liquid phase and also the blending limit of a mixture. The blending region is identified as the area outside the binodal curve.
- Residue curve diagrams for the n-hexane + methanol + pentan-2-one and n-hexane + methanol + 4-methylpentan-2-one systems were successfully predicted from the regressed VLE model parameters and showed the distillation boundaries and nodes to analyse the feasibility of distillation processes. All residue curves originated and terminated at the same two compositions on each diagram and therefore a single distillation region exists for both ternary systems.

- Quaternary data was successfully plotted with the form and arrangement of the binodal surface, separating homogeneous and heterogeneous areas of compositions being demonstrated clearly in a composition tetrahedron.
- Values for the relative selectivity (β) were determined for n-hexane as an extraction solvent in a liquid-liquid extraction process for the separation of methanol + pentan-2-one/4-methylpentan-2-one mixtures. For the ternary mixture, the minimum and maximum β values were 1.23 and 6.41 respectively with the minimum value being for the 4-methylpentan-2-one system and maximum value being for the pentan-2-one system. The β values calculated for the quaternary system were generally lower than those obtained for the ternary systems with a minimum value of 1.06 and maximum value of 2.91.
- For both the ternary and quaternary mixtures, the relative selectivity (β) of n-hexane was greater than unity, indicating that the extraction of the ketones from methanol is feasible using n-hexane, and n-hexane was found to be more selective to pentan-2-one than 4-methylpentan-2-one.

CHAPTER EIGHT

Recommendations

- Additional VLE and LLE measurements of the alkane + alcohol + ketone mixtures should be performed in an expanded range to improve the confidence in the accuracy of the data obtained.
- When conducting VLE measurements, it is imperative to ensure that one increases the internal voltage until the true plateau region is reached especially when oxygenated components are being measured. It is vital that the system operates in the plateau region as operating outside the plateau region would result in inaccurate boiling points, and therefore inaccurate results.
- Thermogreen septa (of significant cost) supplied by Merck were trialled as a liquid seal for sampling in the VLE and LLE equipment. These septa are produced from a rubber formulation and rated for use up to 623 K and vacuum operation. The septa were reported to be compatible with n-hexane but it was found that it was not fully compatible and after a short while of being in contact with n-hexane, the septa began to disintegrate. It is recommended that for any experimental work involving n-hexane, that fully compatible septa are sourced to avoid leaks from equipment and frequent replacement.
- For LLE measurements, it is vital to sample directly from the equilibrium cell and immediately analyse by gas chromatography as evaporation may occur when transferring and storing samples in vials which may lead to inaccurate results.
- In this work, n-hexane was found to be a suitable extraction solvent in the separation of methanol + pentan-2-one/4-methylpentan-2-one mixtures by liquid-liquid extraction. Though, since heavier n-alkanes such as n-heptane or n-octane are less miscible with methanol than n-hexane, these components would likely be better extraction solvents in extraction operations. However, the data presented, with the characteristic interactions, are useful for the design and modelling of applications where mixed n-alkane extraction solvents are employed.

- In this work homogenous blending limits were characterized; however further important fuel blending properties can be estimated using the procedures outlined in Appendix F.

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APPENDIX A

Calibration plots

A.1. Gas Chromatograph

A.1.1 propan-1-ol + n-heptane test system

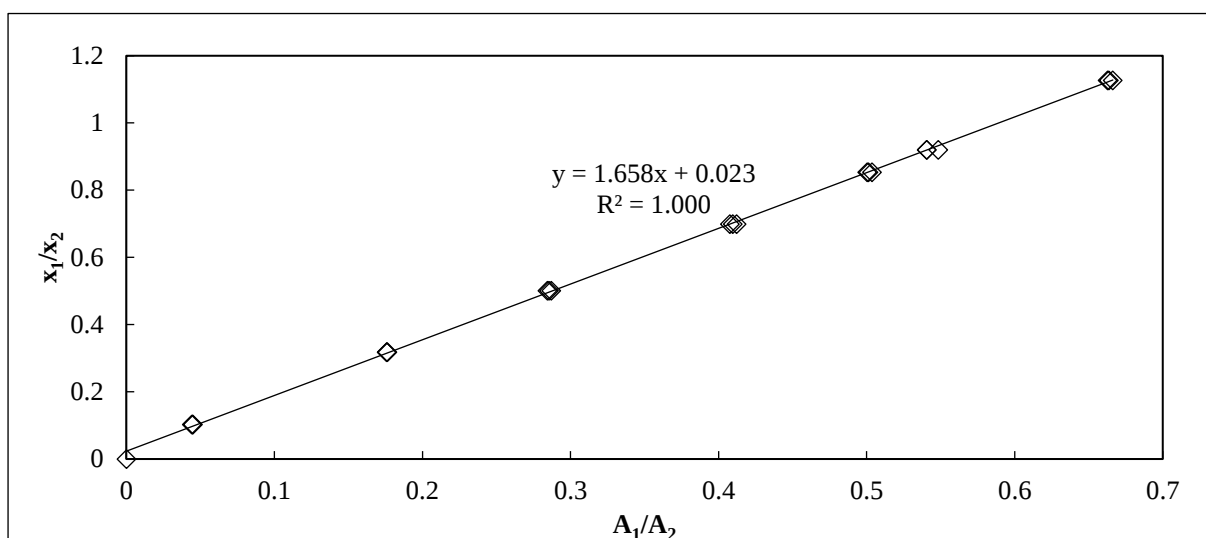


Figure A-1: GC calibration of propan-1-ol (1) + n-heptane (2), propan-1-ol dilute region.

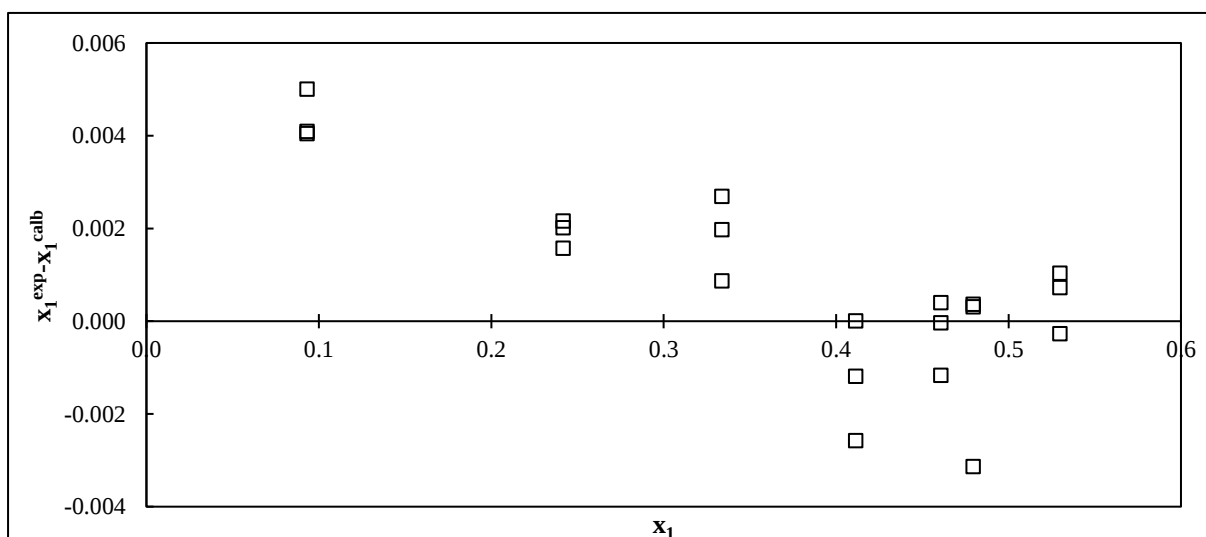


Figure. A-2. Deviation plot for the GC calibration of propan-1-ol (1) + n-heptane (2), propan-1-ol dilute region.

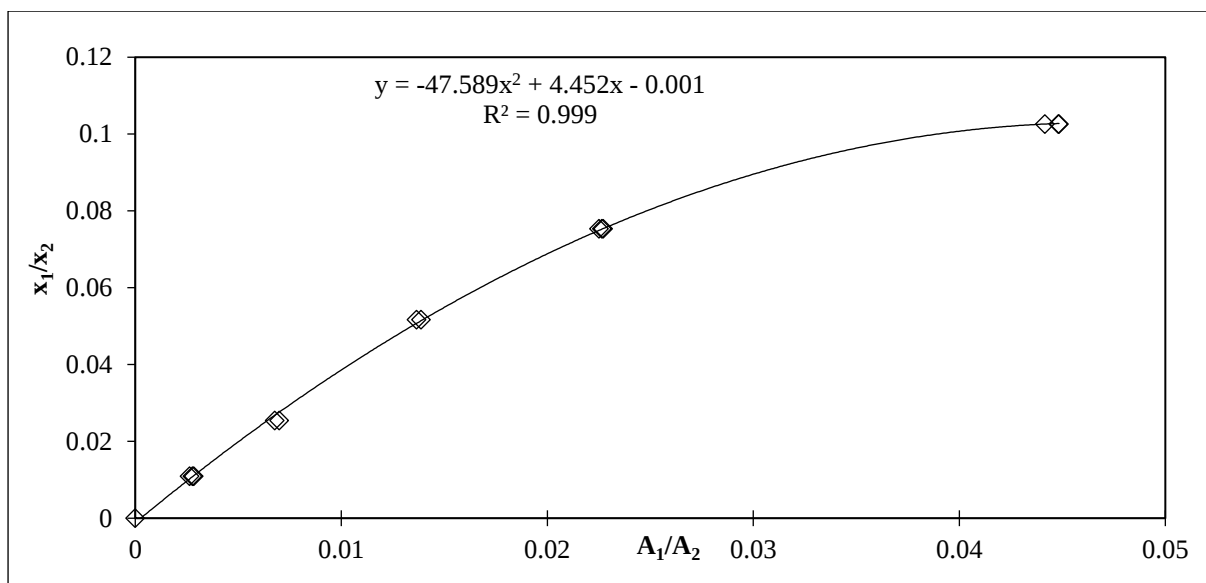


Figure A-3. GC calibration of propan-1-ol (1) + n-heptane (2), propan-1-ol very dilute region.

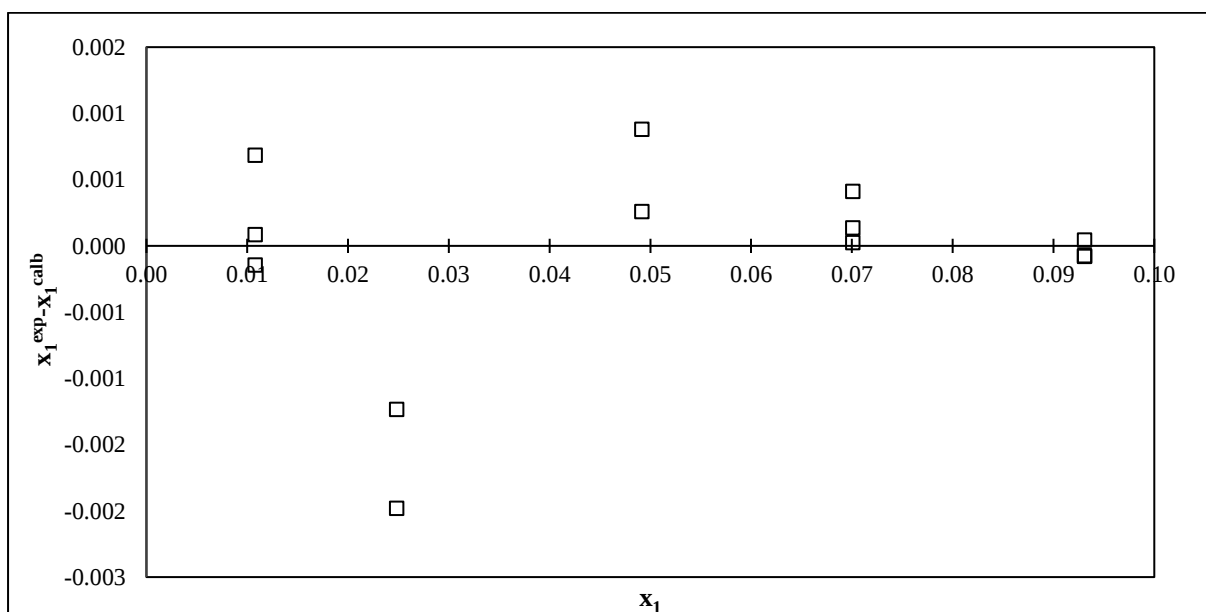


Figure A-4. Deviation plot for the GC calibration of propan-1-ol (1) + n-heptane (2), propan-1-ol very dilute region.

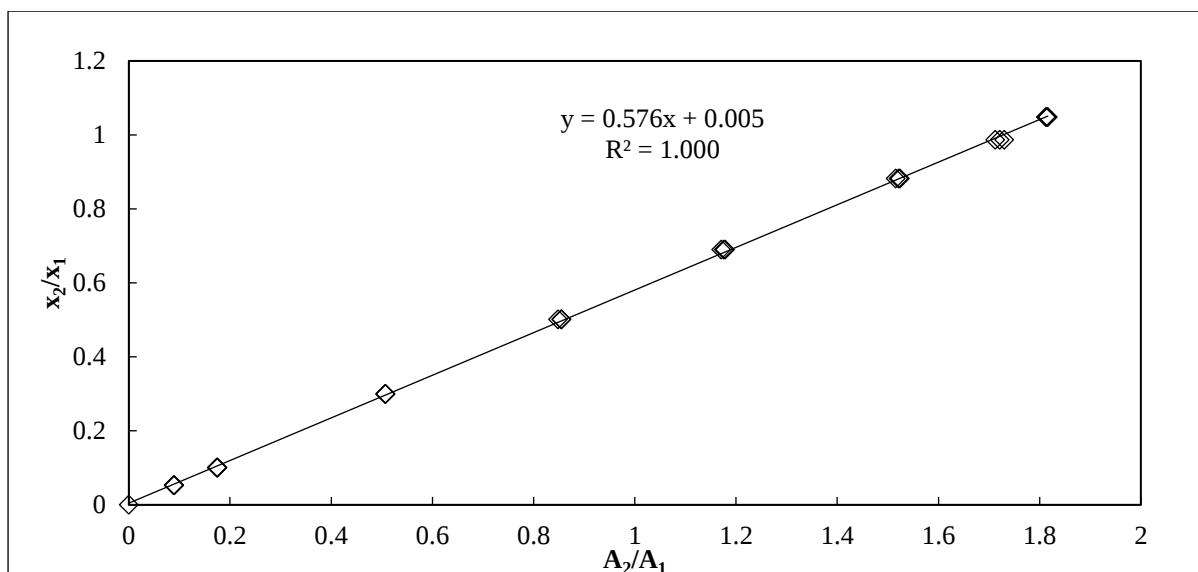


Figure A-5. GC calibration of 1-propan-1-ol (1) + n-heptane (2), n-heptane dilute region.

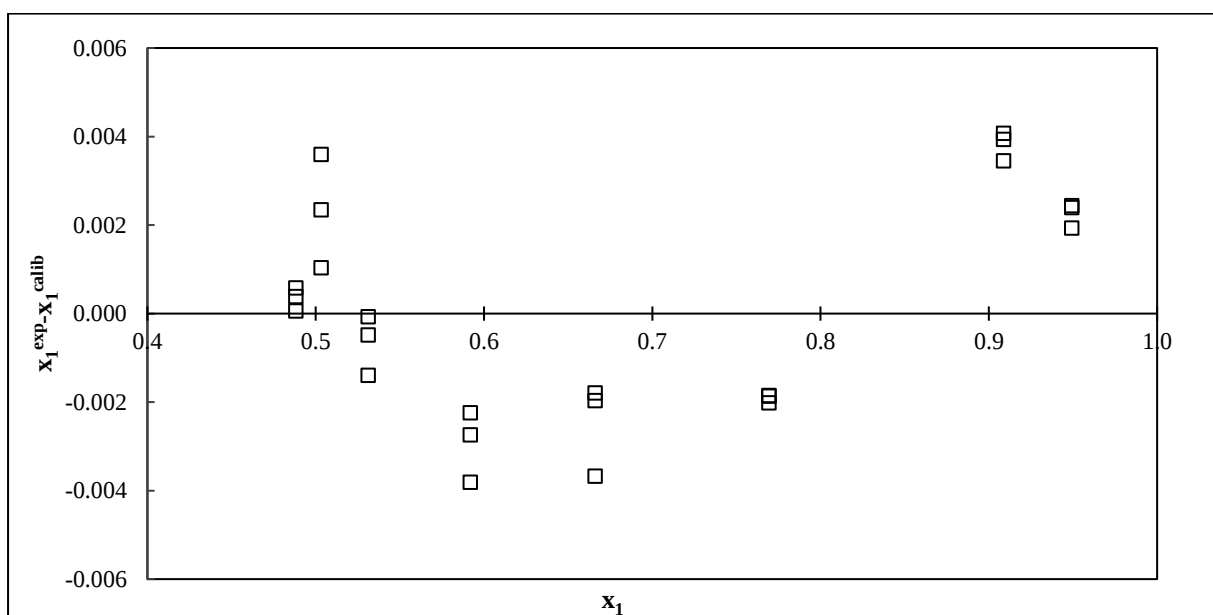


Figure A-6. Deviation plot for the GC calibration of 1-propan-1-ol (1) + n-heptane (2), n-heptane (2) dilute region.

A.1.2 n-hexane + pentan-2-one system

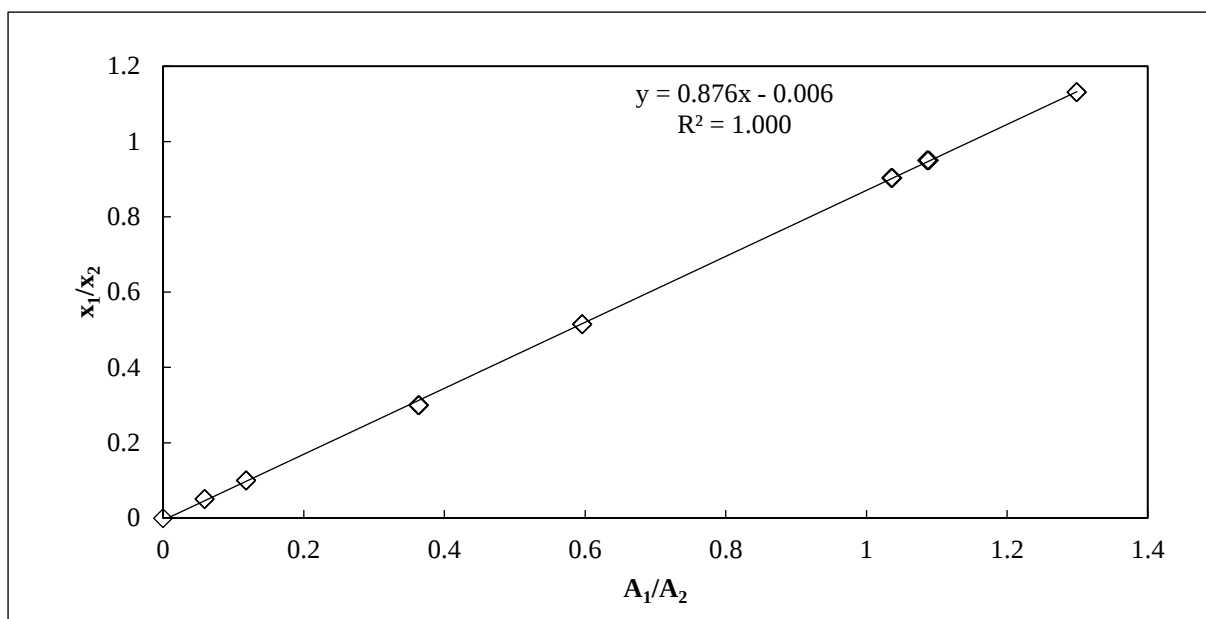


Figure A-7. GC calibration of n-hexane (1) + pentan-2-one (2) system, n-hexane dilute region.

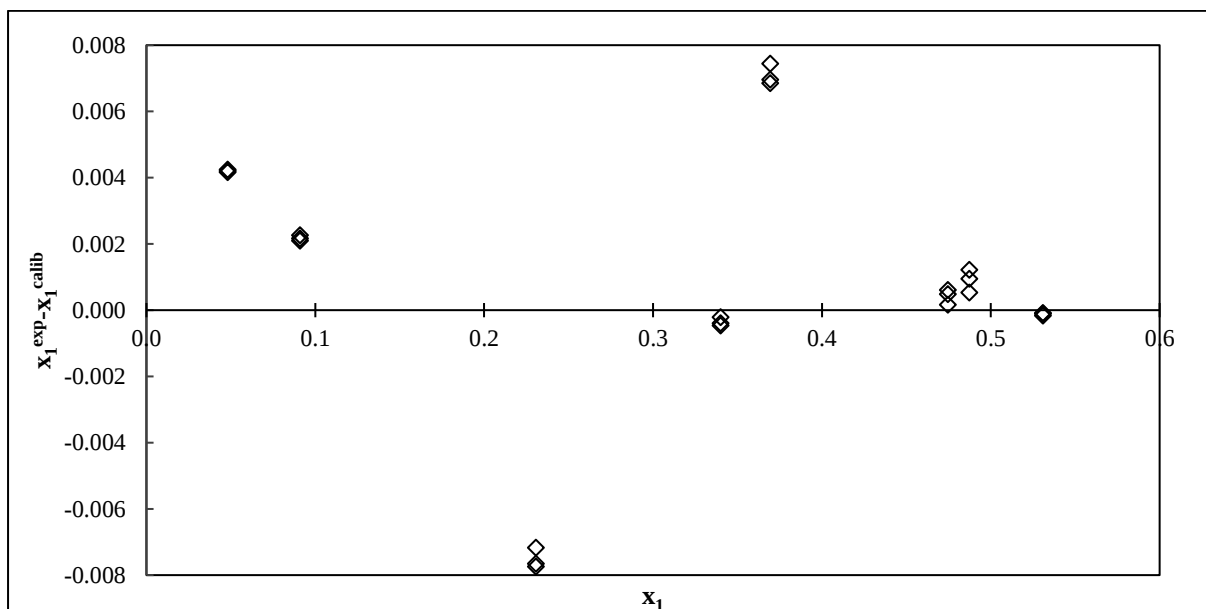


Figure A-8. Deviation plot for the GC calibration of n-hexane (1)+ pentan-2-one (2) system, n-hexane dilute region.

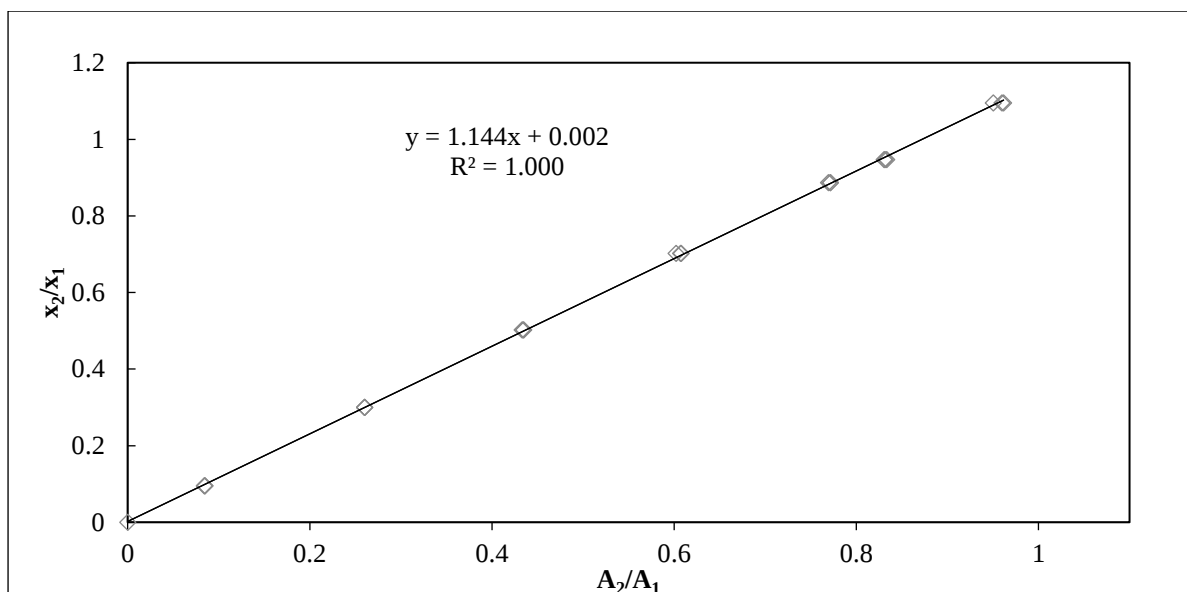


Figure A-9. GC calibration of n-hexane (1) + pentan-2-one (2) system, pentan-2-one system dilute region.

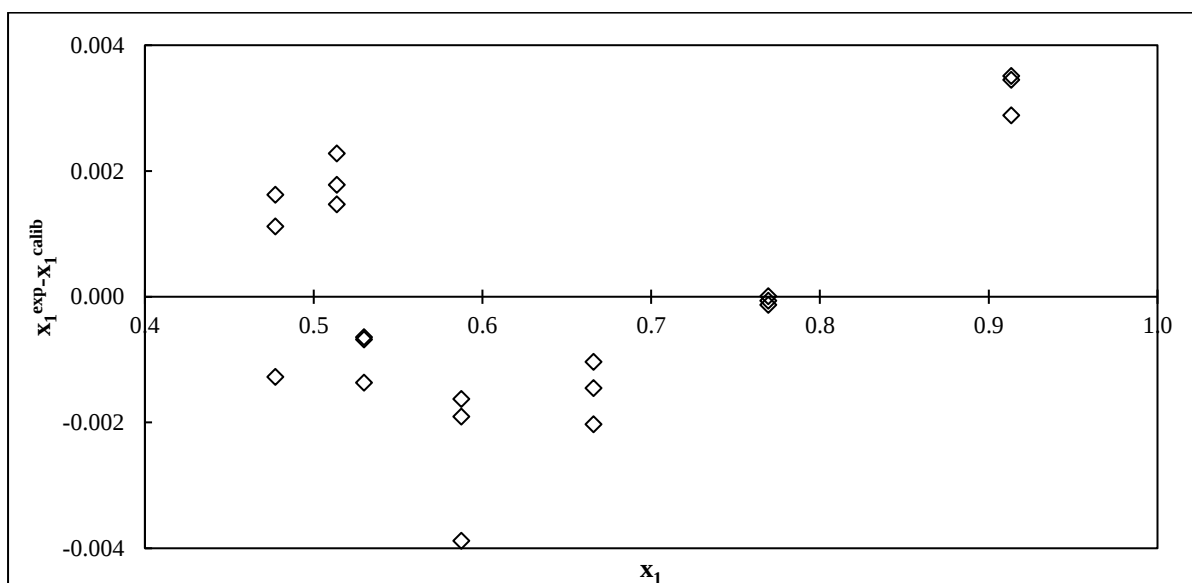


Figure A-10. Deviation plot for the GC calibration of n-hexane (1) + pentan-2-one (2) system, pentan-2-one system dilute region.

A.1.3 n-hexane + 4-methylpentan-2-one system

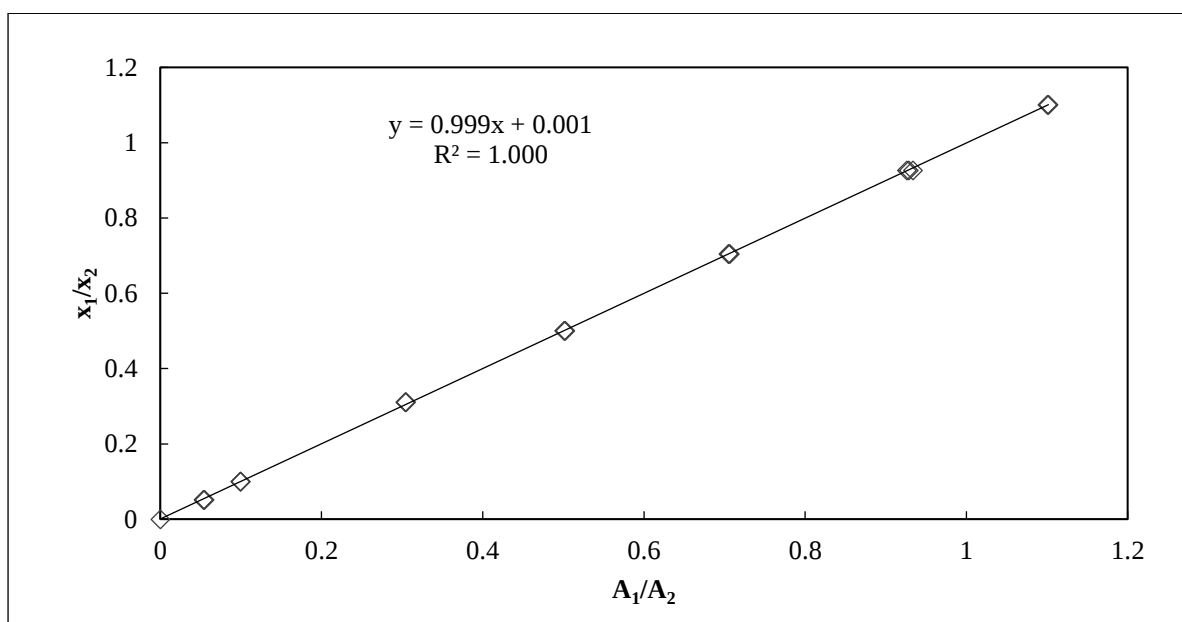


Figure A-11. GC calibration of n-hexane (1) + 4-methylpentan-2-one (2), n-hexane dilute region.

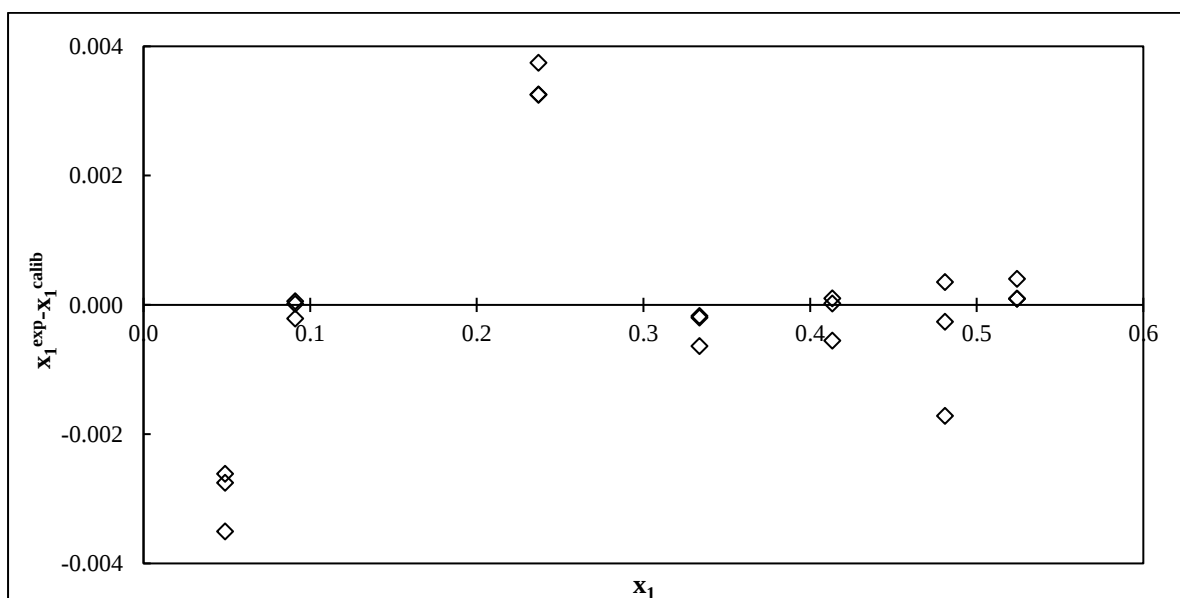


Figure A-12. Deviation plot for the GC calibration of n-hexane (1) + 4-methylpentan-2-one (2), n-hexane dilute region.

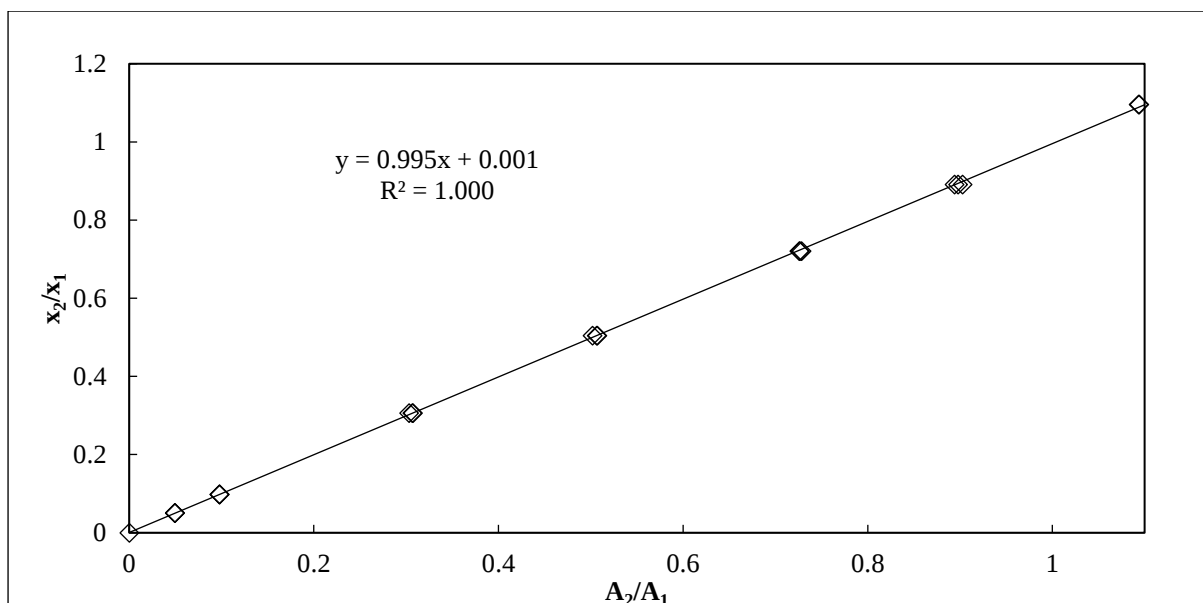


Figure A-13. GC calibration of n-hexane (1) + 4-methylpentan-2-one (2), 4-methylpentan-2-one dilute region.

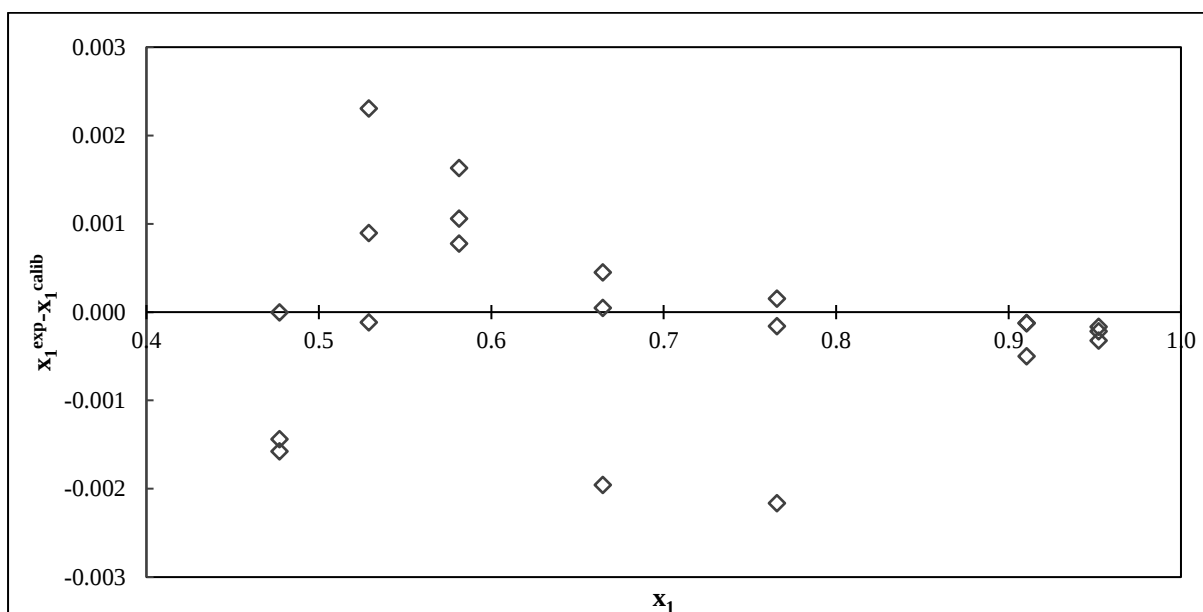


Figure A-14. Deviation plot for the GC calibration of n-hexane (1) + 4-methylpentan-2-one (2), 4-methylpentan-2-one dilute region.

A.1.4 n- hexane + methanol system

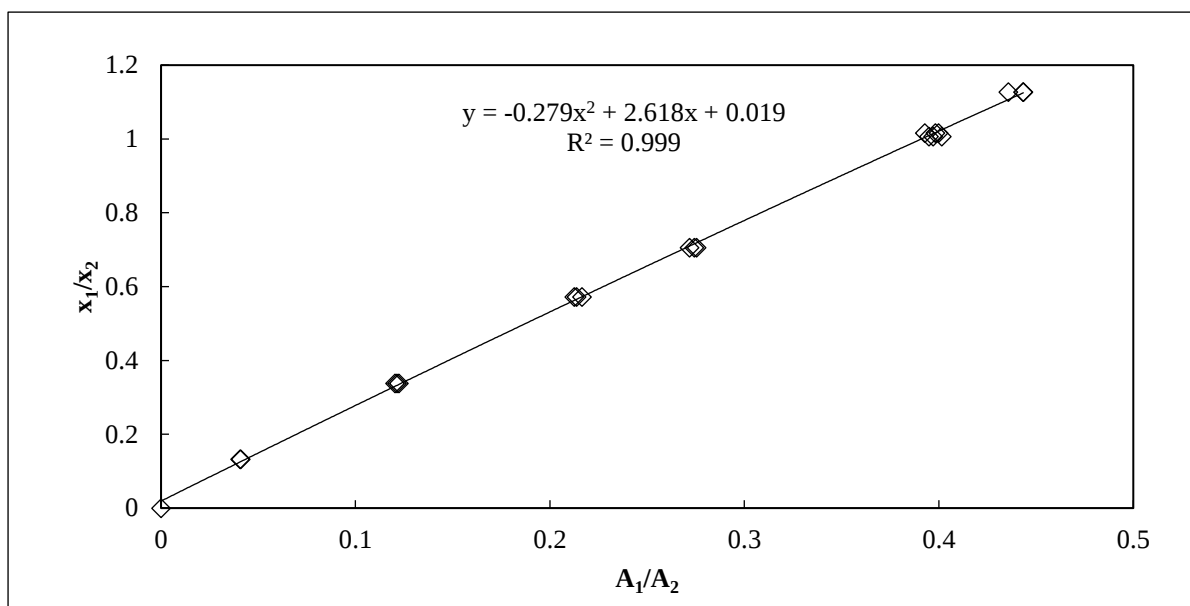


Figure A-15. GC calibration of n-hexane (1) + methanol (2), n-hexane dilute region.

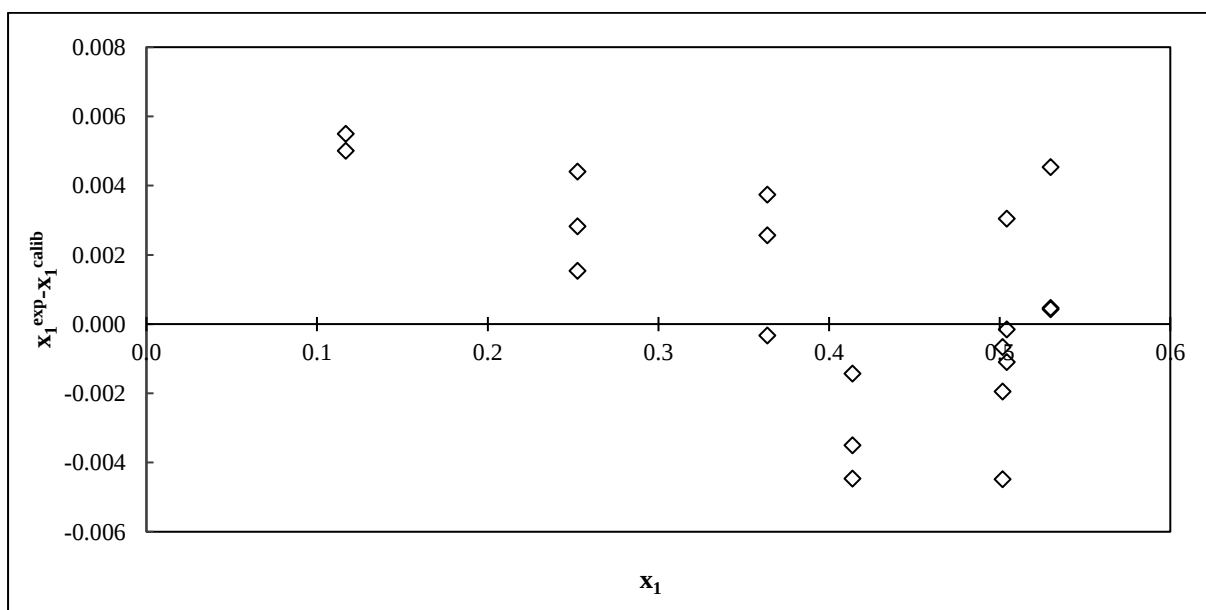


Figure A-16. Deviation plot for the GC calibration of n-hexane (1) + methanol (2), n-hexane dilute region.

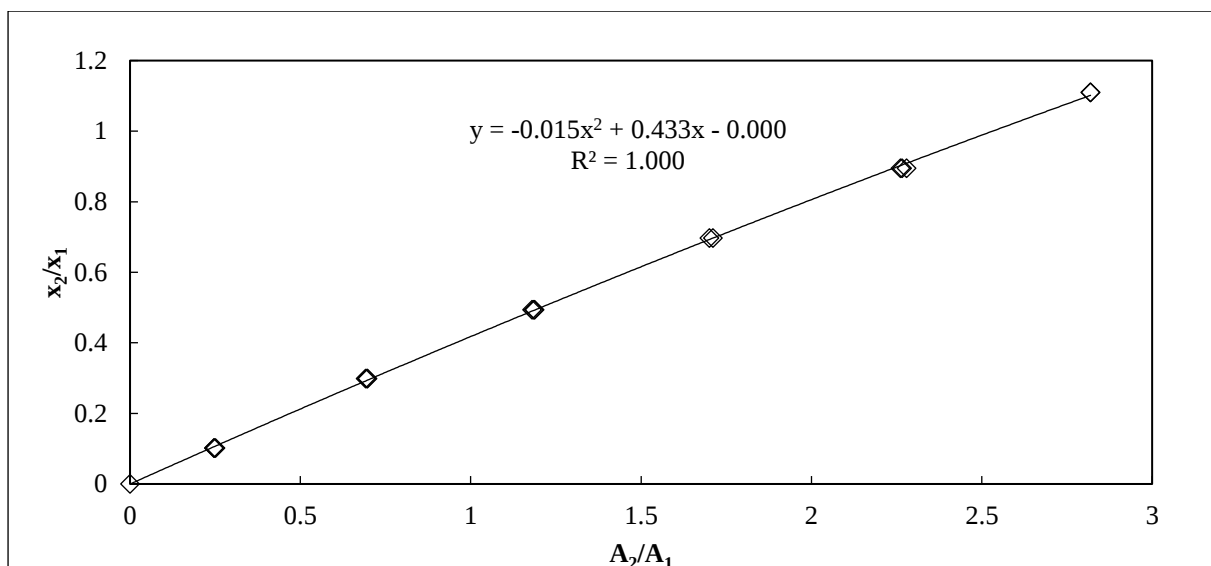


Figure A-17. GC calibration of n-hexane (1) + methanol (2), methanol dilute region.

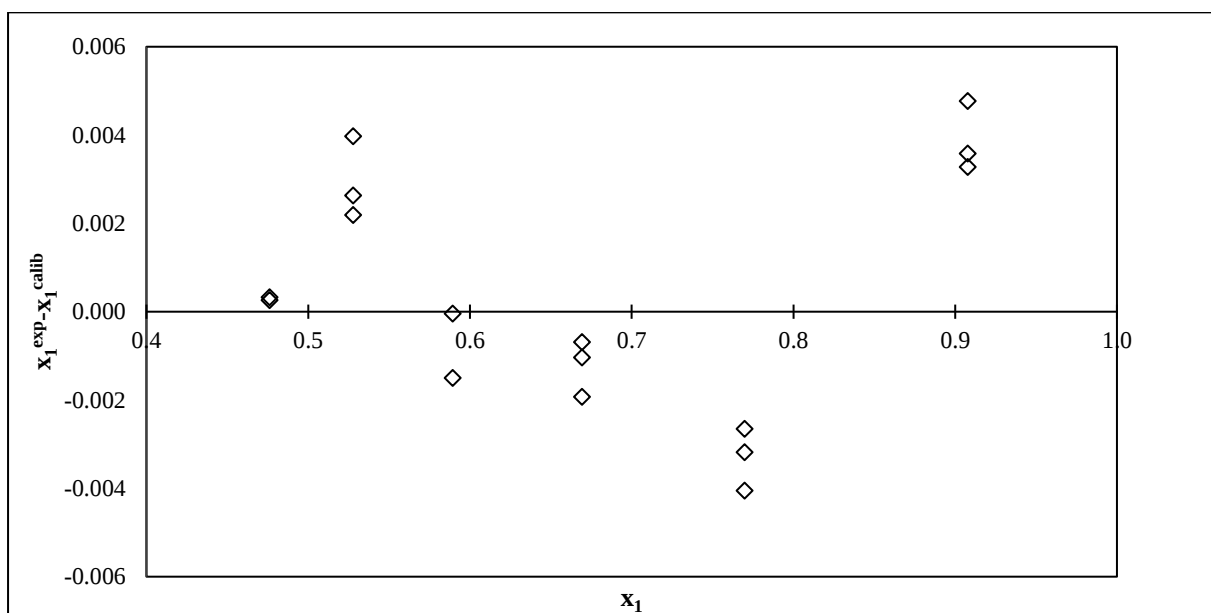


Figure A-18. Deviation plot for the GC calibration of n-hexane (1) + methanol (2), n-hexane dilute region.

A.2 Temperature Calibration

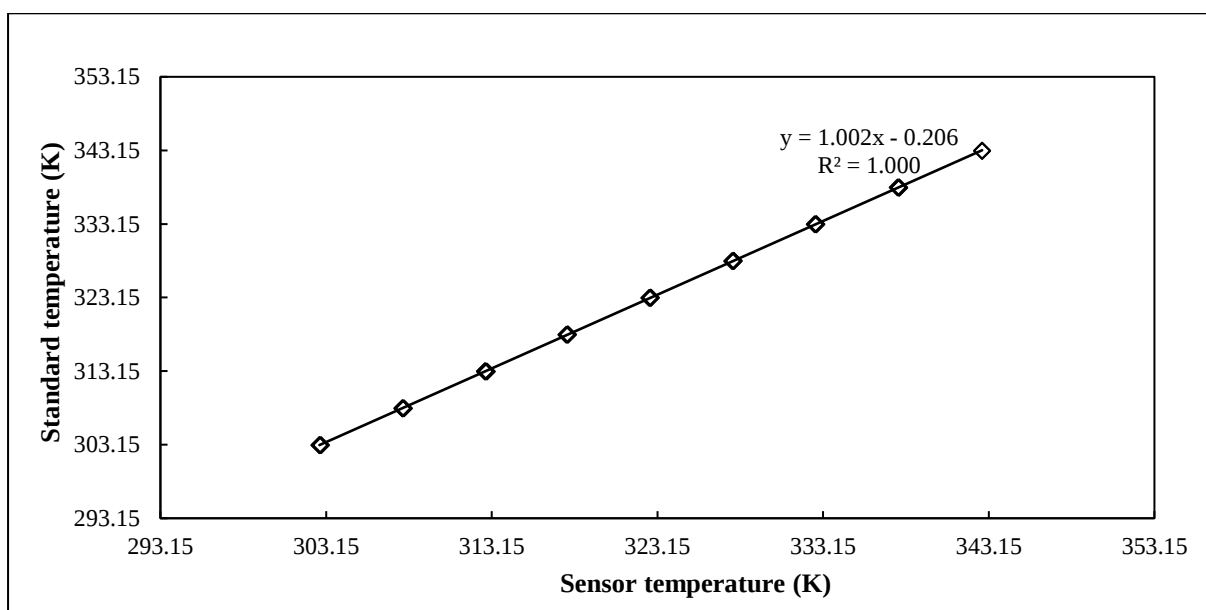


Figure A-19. Temperature calibration of the reference temperature versus the displayed sensor temperature used for VLE measurements.

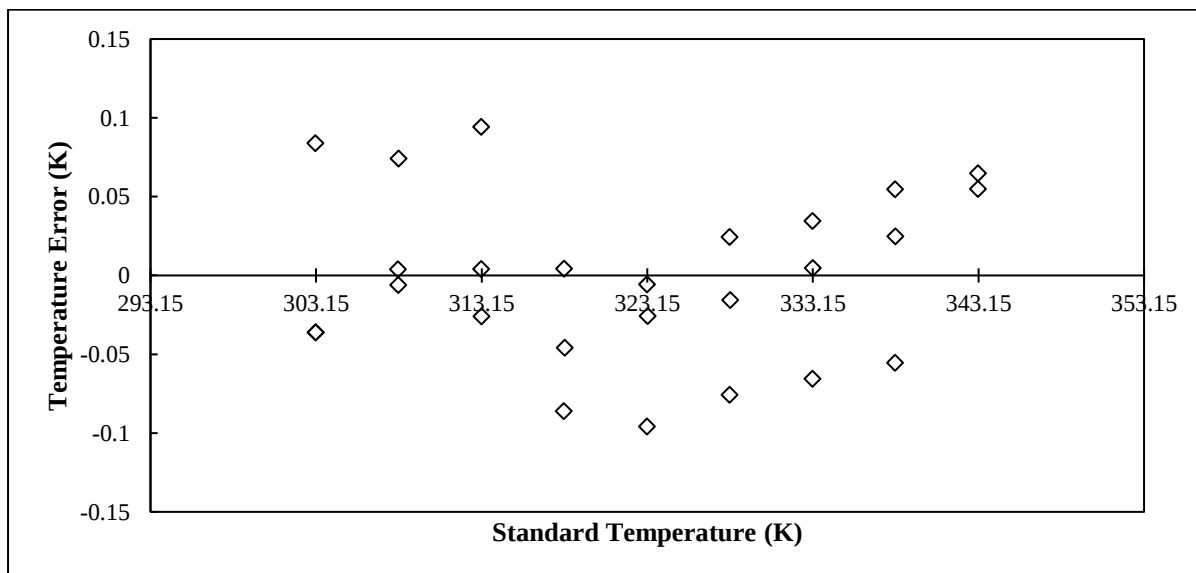


Figure A-20. Deviation plot for temperature calibration for VLE measurements.

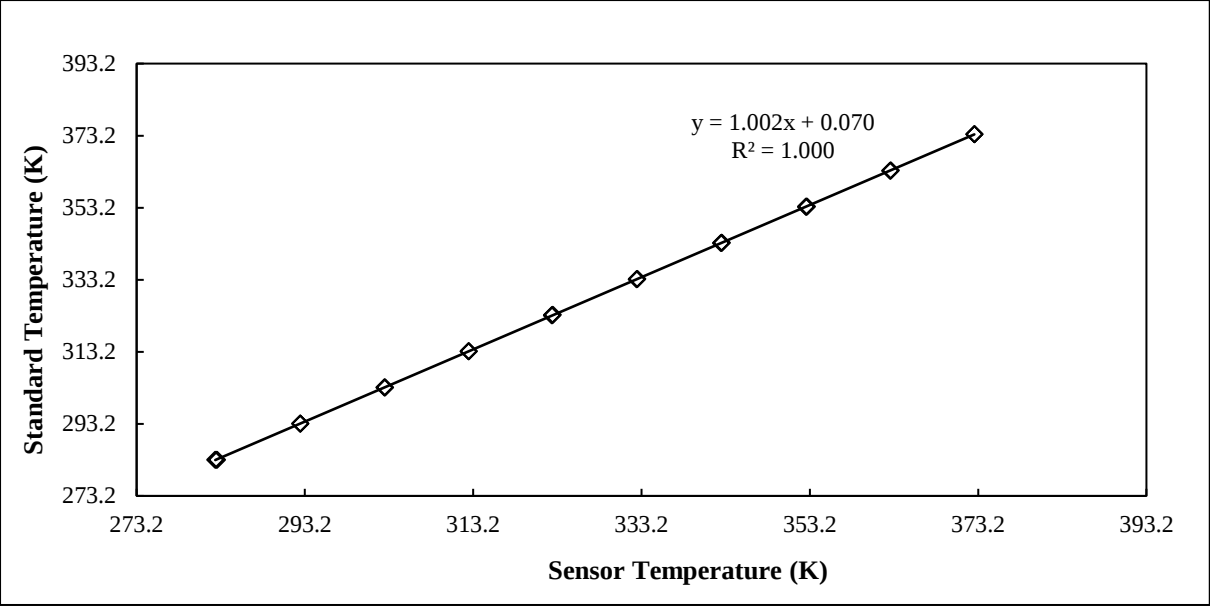


Figure A-21. Temperature calibration of the reference temperature versus the displayed Pt-100 sensor temperature used for LLE measurements.

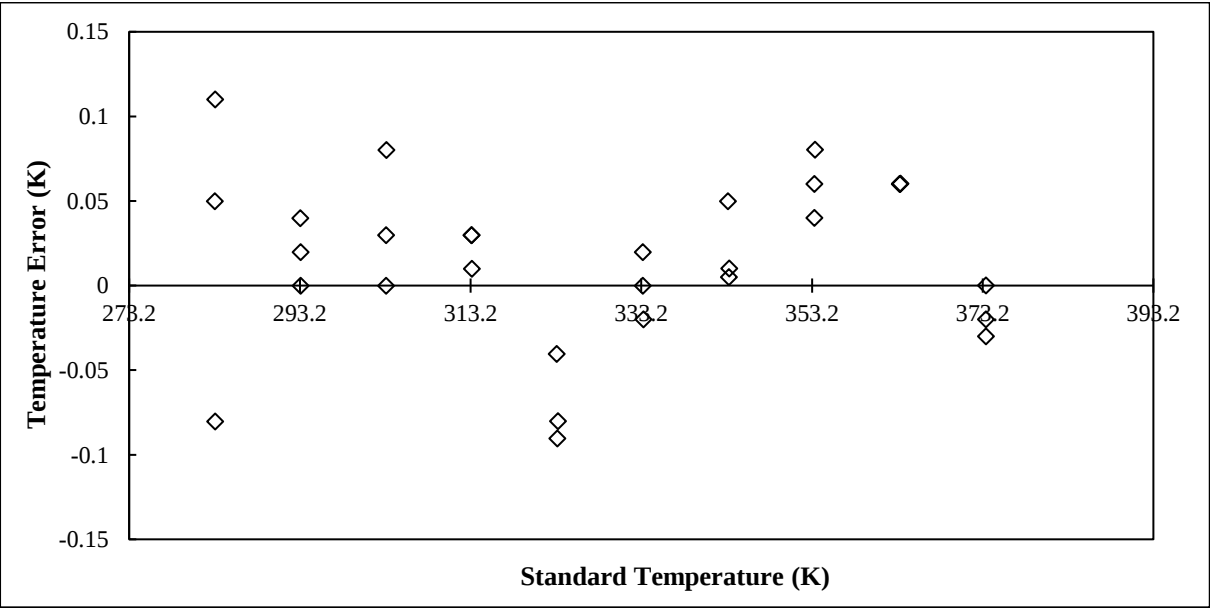


Figure A-22. Deviation plot for temperature calibration for LLE measurements.

A.3 Pressure Calibration for the P-10 transducer for VLE

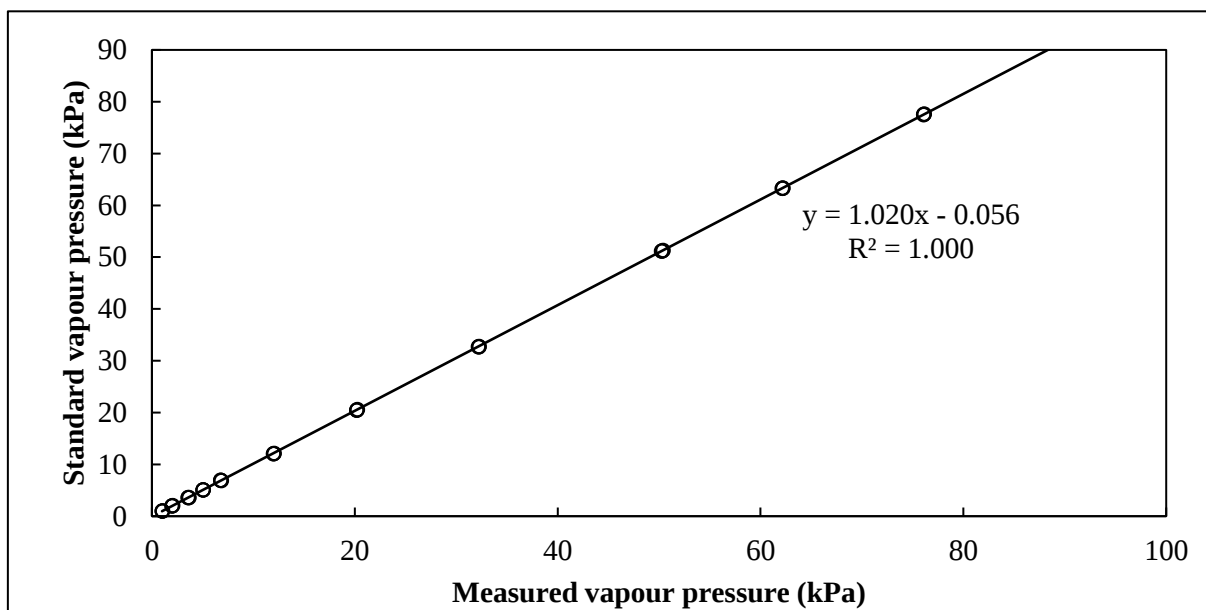


Figure A-23. Pressure calibration of the reference pressure versus the measured pressure.

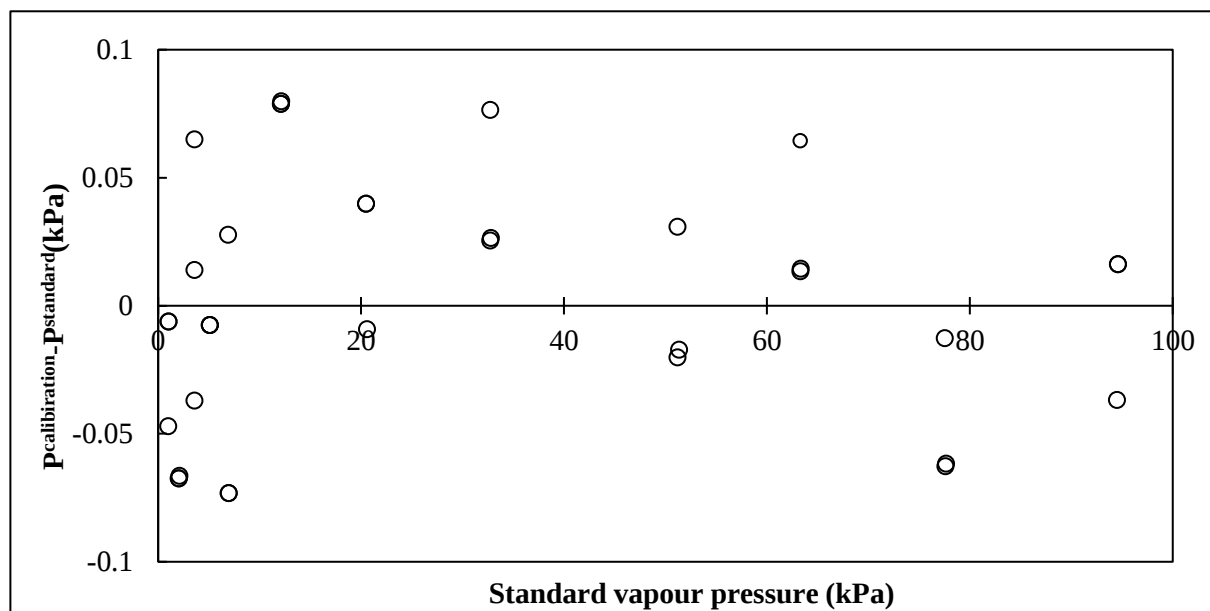


Figure A-24: Deviation plot for pressure calibration.

APPENDIX B:

Uncertainty calculations

Uncertainty gives an indication of the accuracy and precision of the measurements carried out and provides a range in which the true measured value is within. The standard equation representing uncertainty as given by the NIST standard of computing uncertainty (ISO, 2008) is:

$$u_c(\vartheta) = \pm \sqrt{\sum_i u_i(\vartheta)^2} \quad (\text{B-1})$$

where ϑ refers to the quantity being evaluated for uncertainty. All sources of error, including calibration and measuring instruments are taken into account with equation B-1. For this study, uncertainties in pressure, temperature and composition are calculated.

B.1: Pressure and Temperature Uncertainty

The uncertainty in pressure is calculated in the same way as for temperature. The uncertainty for temperature is calculated by the following equation:

$$u_c(T) = \pm \sqrt{u_{\text{calibration}}(T)^2 + u_{\text{repeatability}}(T)^2 + u_{\text{device}}(T)^2} \quad (\text{B-2})$$

These uncertainties are due to deviations in calibration and use of measuring instruments as well as the device uncertainty. The calibration plot, which shows the deviation from the set point temperature, is used to attain the upper and lower limit of uncertainty for the temperature function. The uncertainty calculated in this work is referred to as Type A and B (random) uncertainty

The following equations shows the rectangular distribution using the random approach which applies to calibration and device uncertainty:

$$u_i(T) = \frac{b}{\sqrt{3}} \quad (\text{B-3})$$

The value for b is the error quantity. This is given by the average of the length between the upper and lower limit of the uncertainty in temperature.

Uncertainty in repeatability is measured is also calculated. While sampling, the temperature and pressure at that specific moment is not the same, so it is necessary to calculate the uncertainty in repeatability of measurements. The behaviour of the repeatability in measurements shows a Gaussian distribution. It is assumed that the measurements are expected to fall close to the mean and statistical methods are used to evaluate the data set. Therefore, this is referred to as a systematic uncertainty or type A evaluation.

This is shown as follows:

$$u_{repeatability} = \frac{\sigma}{\sqrt{n}} = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^n (T_i - \bar{T})^2} \quad (\text{B-4})$$

Where n is the number of duplicated measurements

B.2: Molar Composition Uncertainty

The uncertainty from molar composition is due to inaccuracies that occur from GC calibration and the averaging of the areas obtained during sampling.

The equation to calculate the uncertainty is similar to that for temperature and pressure uncertainty.

$$u_c(x_i) = \pm \sqrt{u_{calibration}(x_i)^2 + u_{repeatability}(x_i)^2} \quad (\text{B-5})$$

Where i represents component i . When computing the uncertainty in composition $u(x_i)$ for a specific component, the measurement of other quantities, α_i , is necessary. Therefore, the uncertainty in can be accurately represented by measuring the uncertainty due to the other measurements, α_i .

The root-sum-squared uncertainty is shown for composition as:

$$x_i = f(\alpha_1, \alpha_2, \dots, \alpha_n) \quad (\text{B-6})$$

$$u(x_i) = \sqrt{\left[\left(\frac{\partial x_i}{\partial \alpha_1}\right)_{\alpha_i \neq 1} u(\alpha_1)\right]^2 + \left[\left(\frac{\partial x_i}{\partial \alpha_2}\right)_{\alpha_i \neq 1} u(\alpha_2)\right]^2 + \dots + \left[\left(\frac{\partial x_i}{\partial \alpha_n}\right)_{\alpha_i \neq n} u(\alpha_n)\right]^2} \quad (\text{B-7})$$

Examples of uncertainties include the balance used to weigh samples during preparation of standard solutions, any loss to evaporation and handling, purity etc. The symbol B in the following equation represents this factor:

$$u_{\text{calibration}}(x_i) = \sqrt{u_B(x_i)^2 + u_{\text{corr}}(x_i)^2} \quad (\text{B-8})$$

x_i is dependent on the masses of the components in the system, thus, the mole fractions may be expressed in terms of masses of the species involved as follows:

$$u_B(x_i) = \sqrt{\left[\left(\frac{\partial x_i}{\partial m_1}\right)_{m_2} u(m_1)\right]^2 + \left[\left(\frac{\partial x_i}{\partial m_2}\right)_{m_1} u(m_2)\right]^2} \quad (\text{B-9})$$

Using standard relationships: $x_i = \frac{n_i}{(n_i + n_j)}$ and $n_i = \frac{m_i}{MM_i}$

Equation B-9 is reduced to:

$$u_B(x_i) = x_1 x_2 \sqrt{\left(\frac{u(m_1)}{m_2}\right)^2 + \left(\frac{u(m_2)}{m_2}\right)^2} \quad (\text{B-10})$$

APPENDIX C

Test system measurements

C.1. VLE propan-1-ol (1) + heptane (2) test system

Table C-1: P-x-y data for the propan-1-ol (1) + heptane (2) system at 333.2 K

Pressure (kPa)	x ₁	y ₁
28.3	0.000	0.000
30.2	0.007	0.079
30.7	0.009	0.091
31.1	0.010	0.096
33.6	0.018	0.141
34.8	0.026	0.177
37.4	0.066	0.245
37.5	0.071	0.252
38.6	0.091	0.276
39.5	0.137	0.318
39.7	0.163	0.329
39.8	0.191	0.331
39.95	0.231	0.337
40	0.238	0.340
40.2	0.264	0.347
40.5	0.309	0.358
40.6	0.331	0.362
40.7	0.385	0.371
40.65	0.441	0.385
40.6	0.469	0.393
40.4	0.554	0.407
40	0.611	0.418
39.4	0.677	0.436
38.7	0.732	0.452
37.5	0.784	0.484
36.2	0.820	0.515
34.7	0.863	0.550
31.3	0.915	0.625
27.7	0.949	0.712
25.6	0.966	0.790
25.4	0.966	0.782
22.7	0.985	0.903
21.8	0.990	0.943
21.3	0.993	0.971
20.6	1.000	1.000

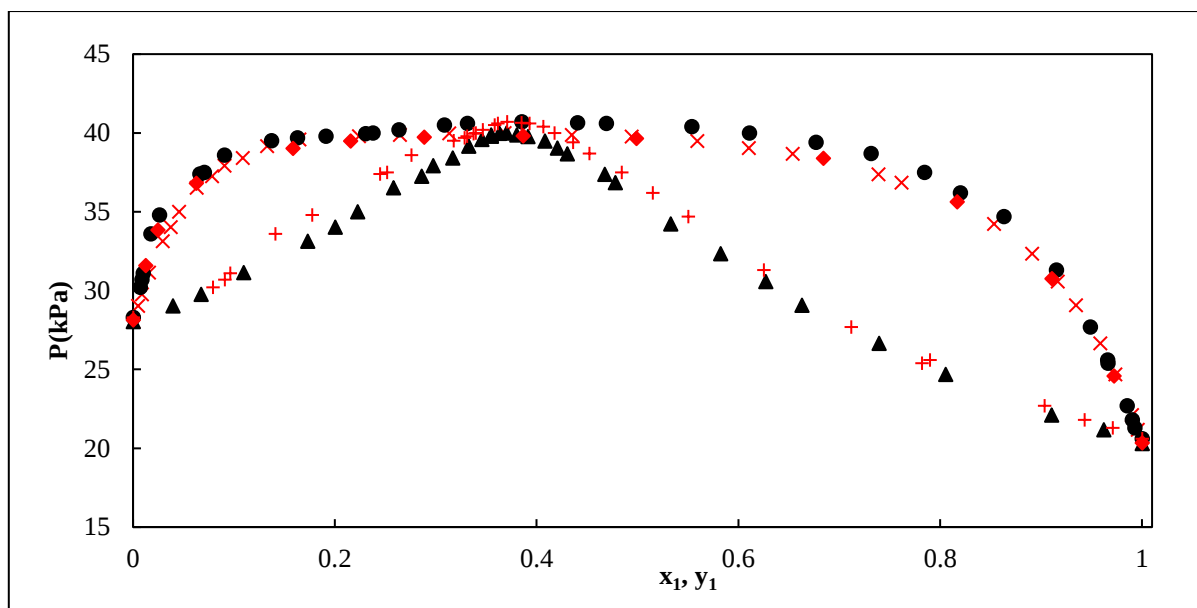


Figure C-1. P-x-y data for the propan-1-ol (1) + heptane (2) system at 333.2 K. ●- experimental x_1 , ▲-experimental y_1 . ×- x_1 and +- y_1 of (Pena and Cheda, 1970) at 333.13 K, ♦ of (Van Ness et al., 1967) at 333.12 K.

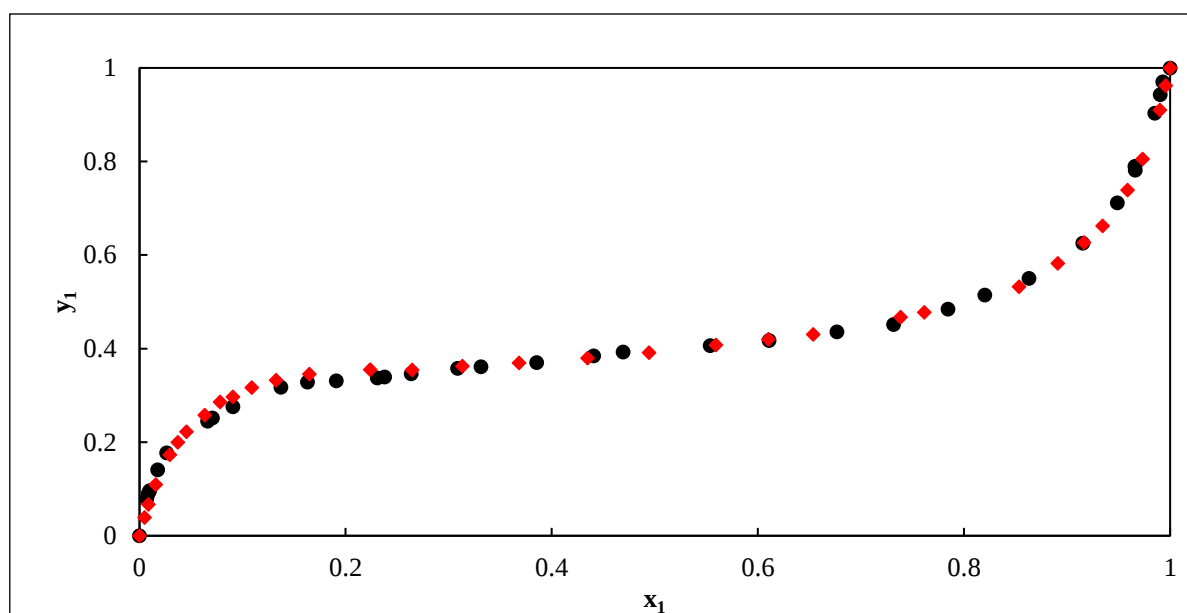


Figure C-2. x-y data for the propan-1-ol (1) + heptane (2) system at 333.2 K. ●- experimental. ♦- data of (Pena and Cheda, 1970) at 333.13 K.

C.2. LLE methanol (1) + n-hexane (2) binary test system

Table C-2: Binary liquid-liquid equilibrium data for methanol (1) + n-hexane (2) at 0.1MPa.^a

T/ K	Lower phase		Upper phase	
	methanol (x ₁)	n-hexane (x ₂)	methanol (x ₁)	n-hexane (x ₂)
300.3	0.790	0.210	0.271	0.729
303.2	0.758	0.243	0.321	0.679
303.4	0.746	0.254	0.333	0.667
307.3	0.668	0.332	0.428	0.572
308.1	0.644	0.356	0.463	0.537
309.0	0.492	0.508	0.603	0.397

^a Standard combined uncertainties uc are uc (T) = 0.1 K, uc (P) = 1 kPa, uc(xi) = 0.005

C.2. LLE methanol (1) + n-hexane (2) binary test system

Table C-2: Binary liquid-liquid equilibrium data for methanol (1) + n-hexane (2) at 0.1MPa.^a

T/ K	Lower phase		Upper phase	
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309.0	0.492	0.508	0.603	0.397

^a Standard combined uncertainties uc are uc (T) = 0.1 K, uc (P) = 1 kPa, uc(xi) = 0.005

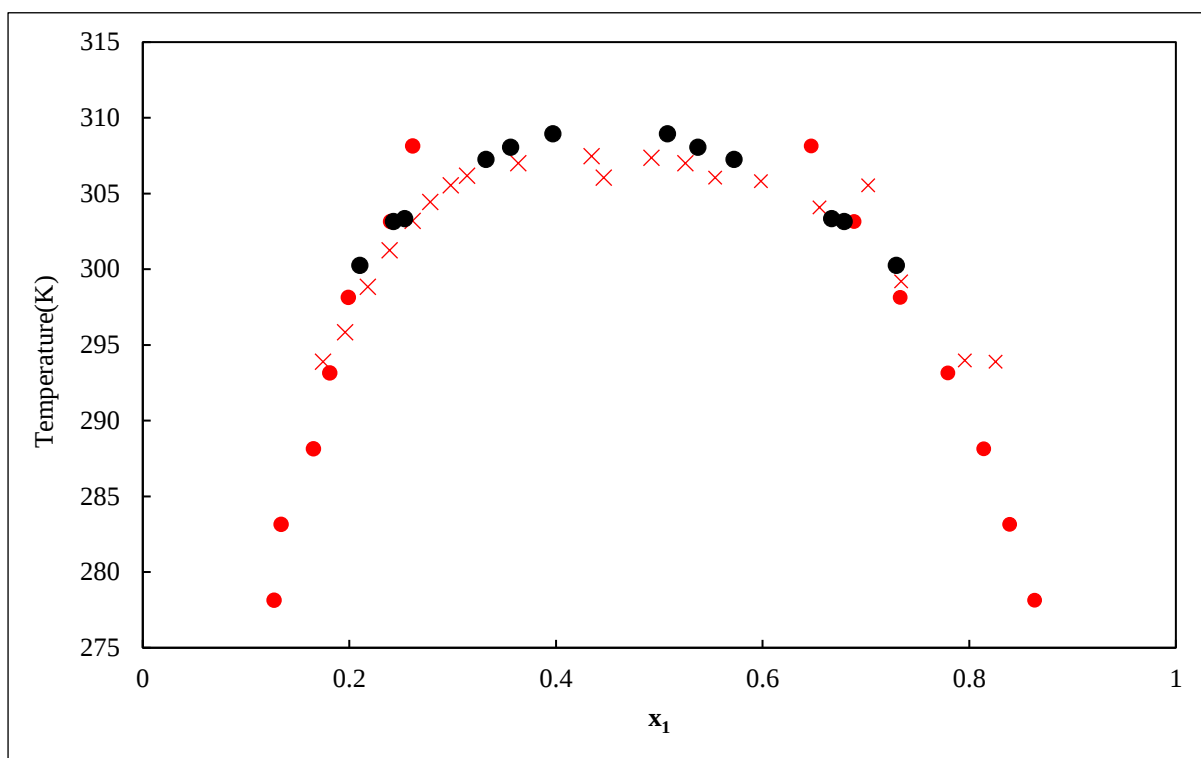


Figure C-3. Comparison of Binary LLE experimental data of the methanol (1) + n-hexane (2) system to literature data at 0.1MPa. ●-experimental x_1 , ×- x_1 of (Blanco and Ortega, 1996), ●- x_1 of (Orge et al., 1997).

APPENDIX D

x-y plots for VLE systems

D.1 n-hexane (1) + pentan-2-one (2) system

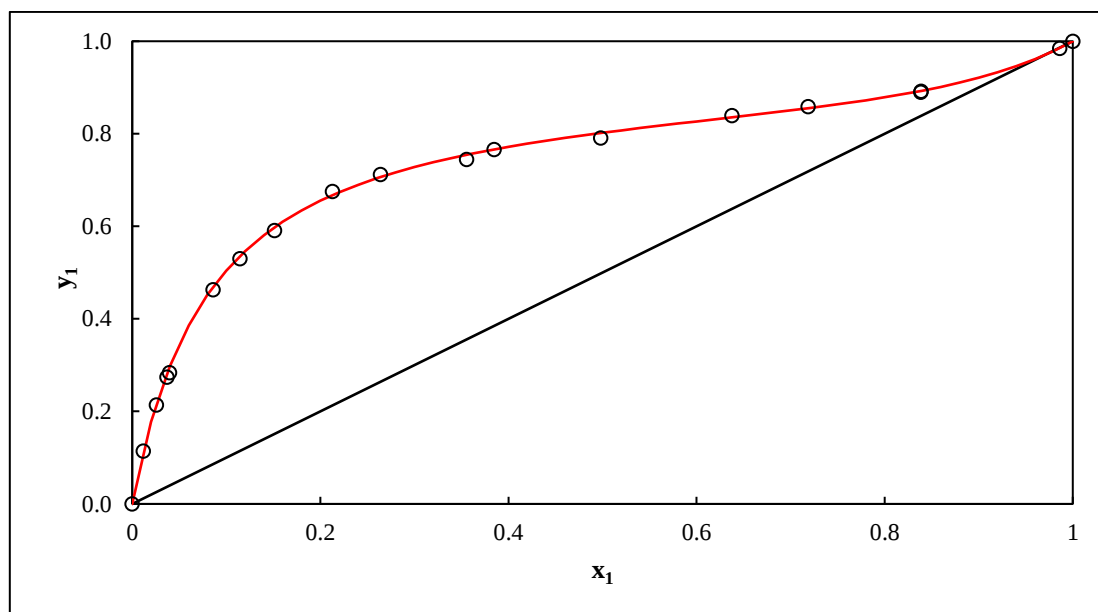


Figure D-1. x_1 - y_1 plot for the n-hexane (1) + pentan-2-one (2) system at 313.2K. (xy- o)
Experimental data, (xy- —) UNIQUAC-HOC model data.

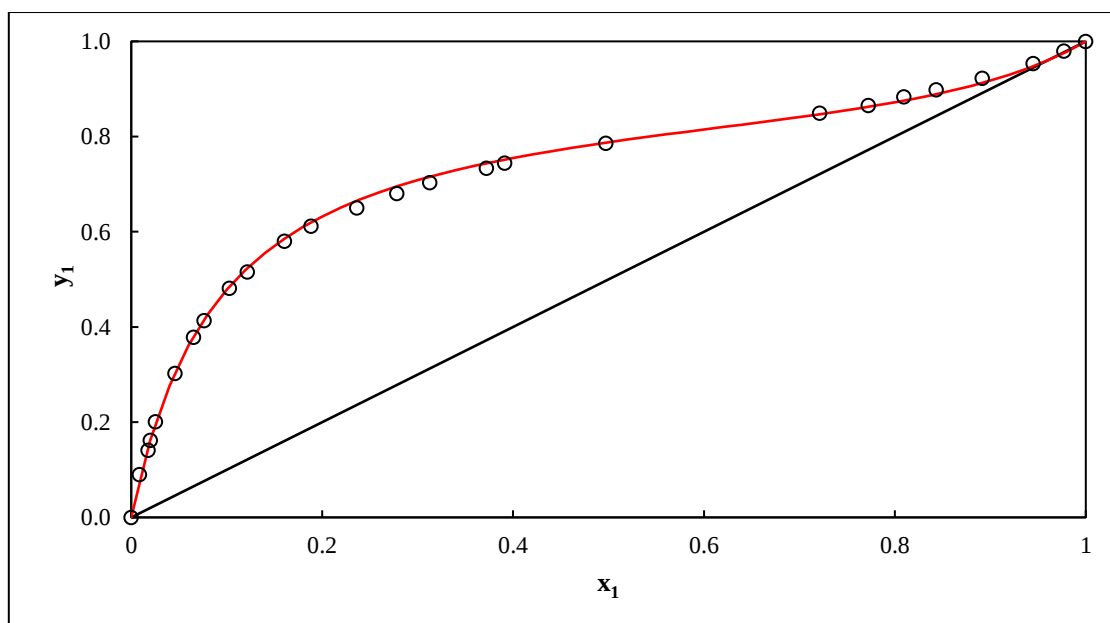


Figure D-2. x_1 - y_1 plot for the n-hexane (1) + pentan-2-one (2) system at 323.2K. (xy- o)
Experimental data, (xy- —) UNIQUAC-HOC model data.

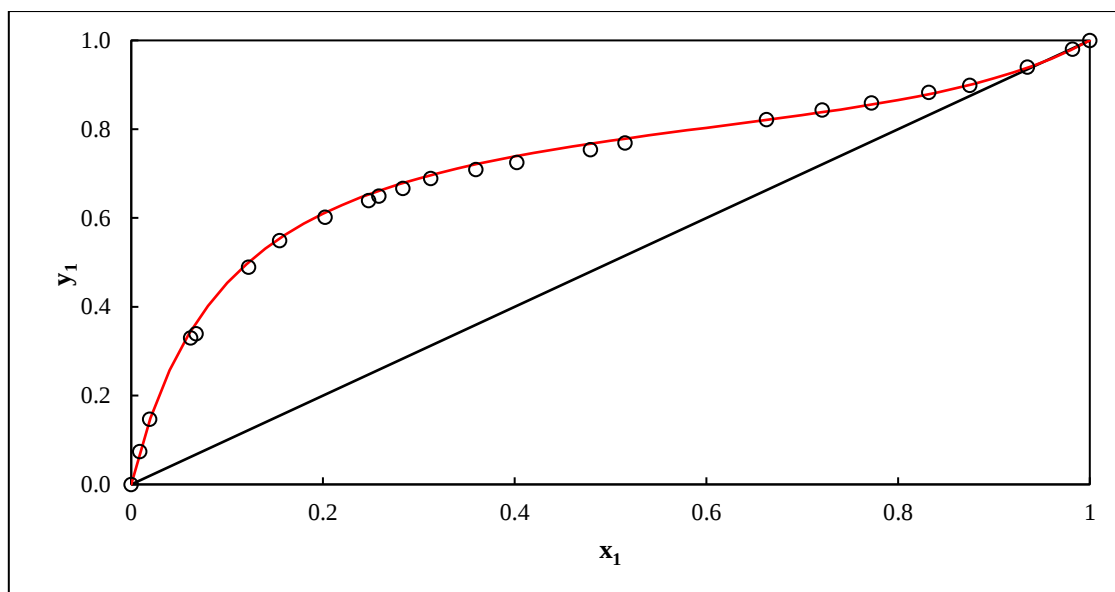


Figure D-3. x_1 - y_1 plot for the n-hexane (1) + pentan-2-one (2) system at 333.2K. (xy- o) Experimental data, (xy —) UNIQUAC-HOC model data.

D.2 n-hexane (1) + 4-methylpentan-2-one (2) VLE system

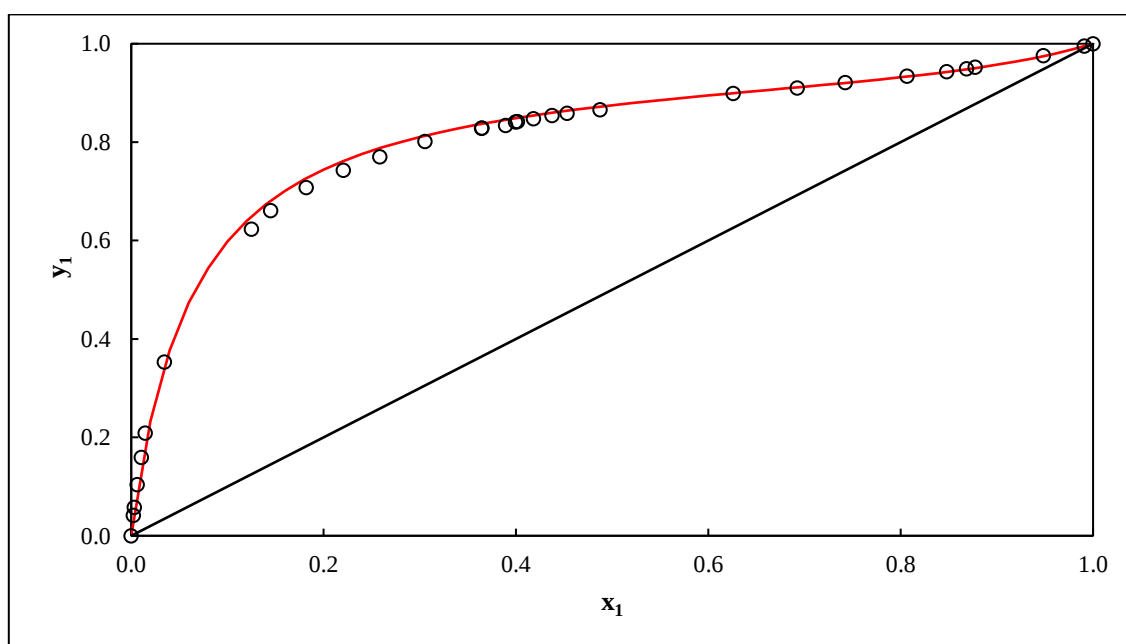


Figure D-4. x_1 - y_1 plot for the n-hexane (1) + 4- methylpentan-2-one (2) system at 313.2K. (xy- o) Experimental data, (xy —) UNIQUAC-HOC model data.

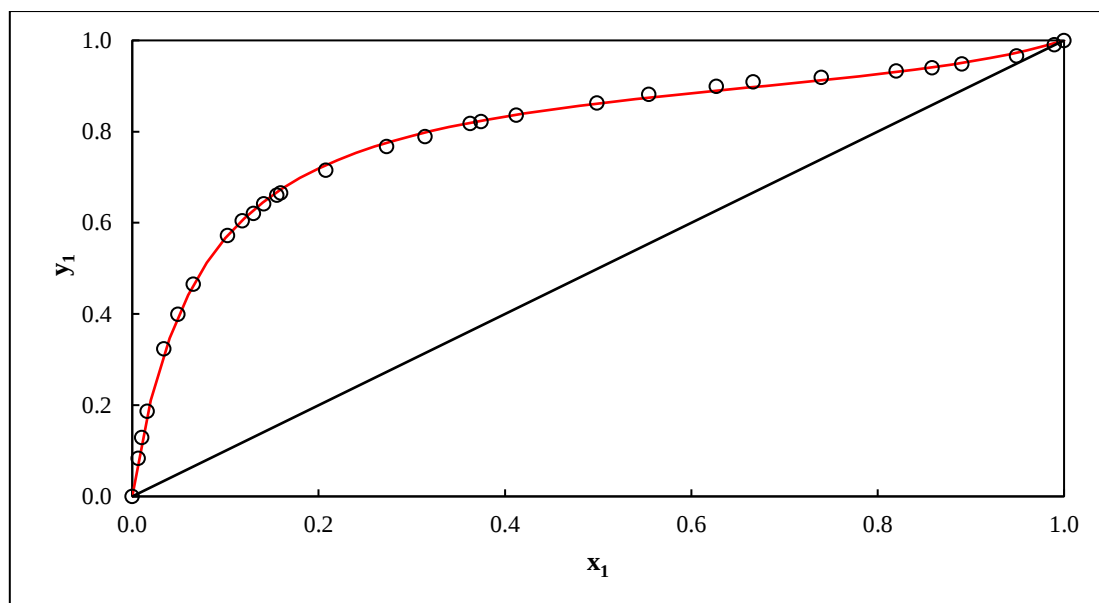


Figure D-5. x_1 - y_1 plot for the n-hexane (1) + 4-methylpentan-2-one (2) system at 323.2K.
(xy- o) Experimental data, (xy- —) UNIQUAC-HOC model data.

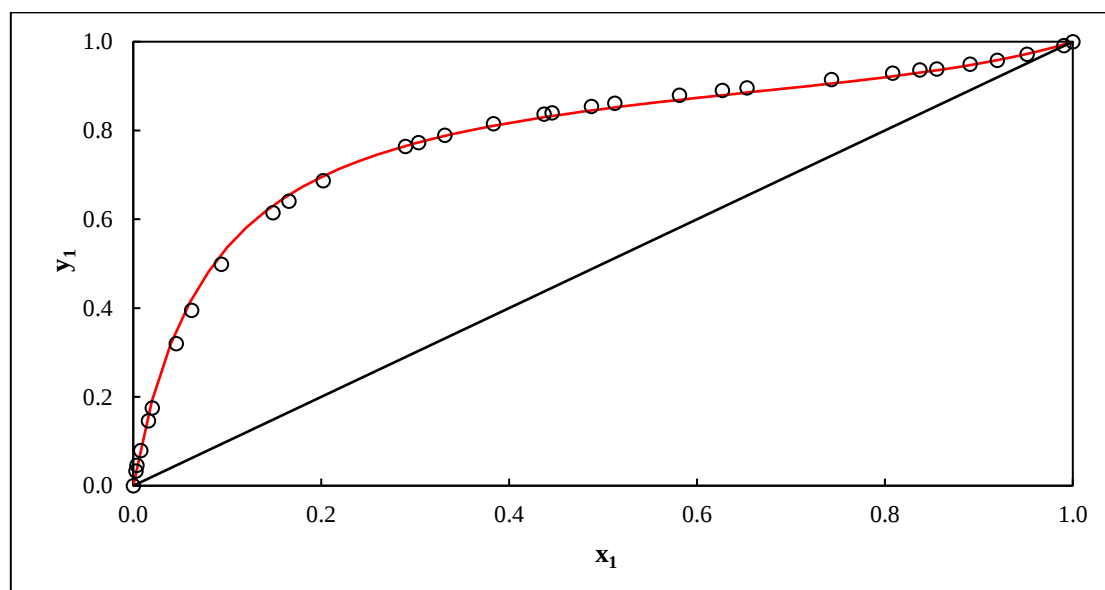


Figure D-6. x_1 - y_1 plot for the n-hexane (1) + 4-methylpentan-2-one (2) system at 333.2K.
(xy- o) Experimental data, (xy- —) UNIQUAC-HOC model data.

APPENDIX E

Results of the Thermodynamic Consistency Tests

E1. n-hexane (1) + pentan-2-one (2) VLE system

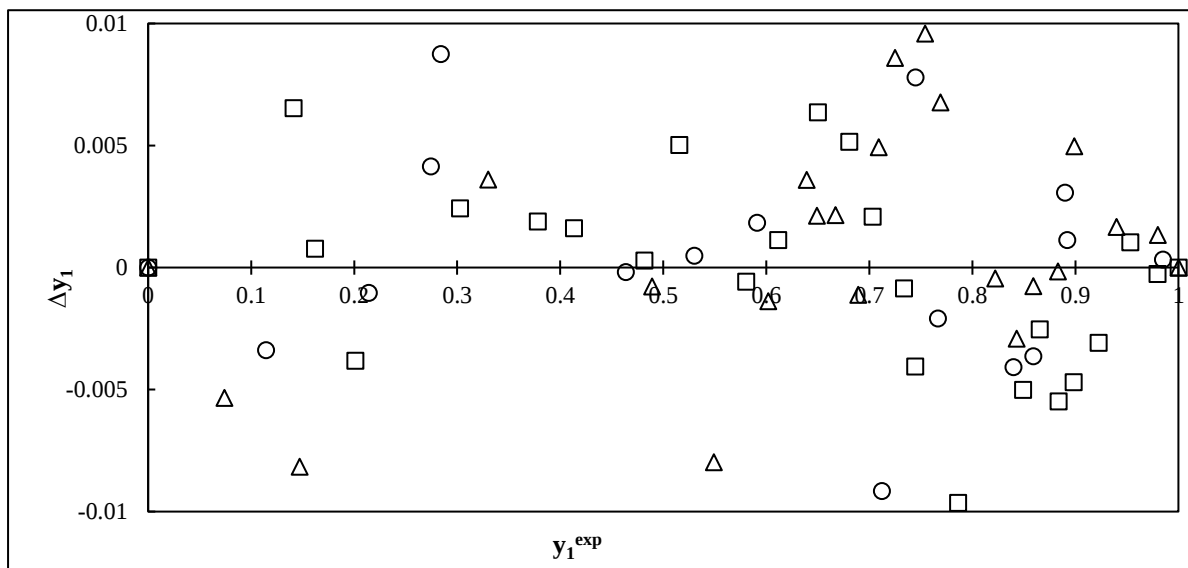


Figure E-1. Plot of deviations in y for the n-hexane (1) + pentan-2-one (2) system at ($\circ$ -313.3, $\square$ -323.3 and $\triangle$ -333.5) K using the point test of (Christiansen and Fredenslund, 1975).

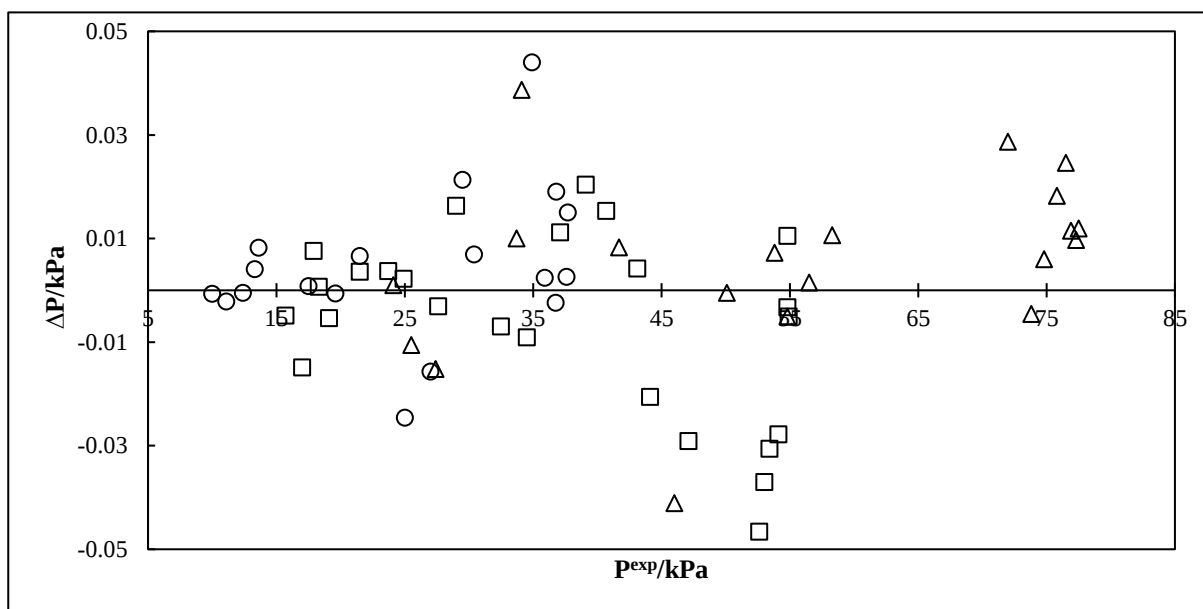


Figure E-2. Plot of deviations in P for the n-hexane (1) + pentan-2-one (2) system at ($\circ$ -313.3, $\square$ -323.3 and $\triangle$ -333.5) K using the point test of (Christiansen and Fredenslund, 1975).

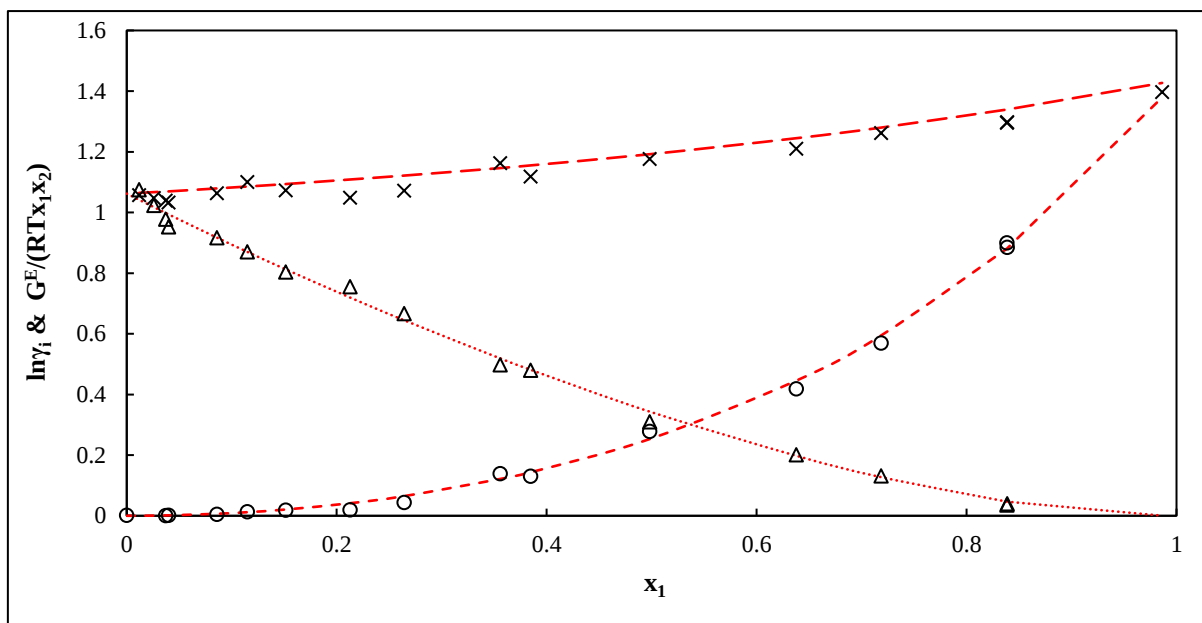


Figure E-3. Plot of $\ln\gamma_i$ ($\ln\gamma_1$ - Δ , $\ln\gamma_2$ - $\circ$) & $G^E/(RTx_1x_2)$ ($\times$) for the n-hexane (1) + pentan-2-one (2) system at 313.3 K using the infinite dilution test of (Kojima et al., 1990) and the UNQUAC-HOC model ($\ln\gamma_1$ - $\cdots$, $\ln\gamma_2$ - $---$, $G^E/(RTx_1x_2)$ - $-\cdot-$).

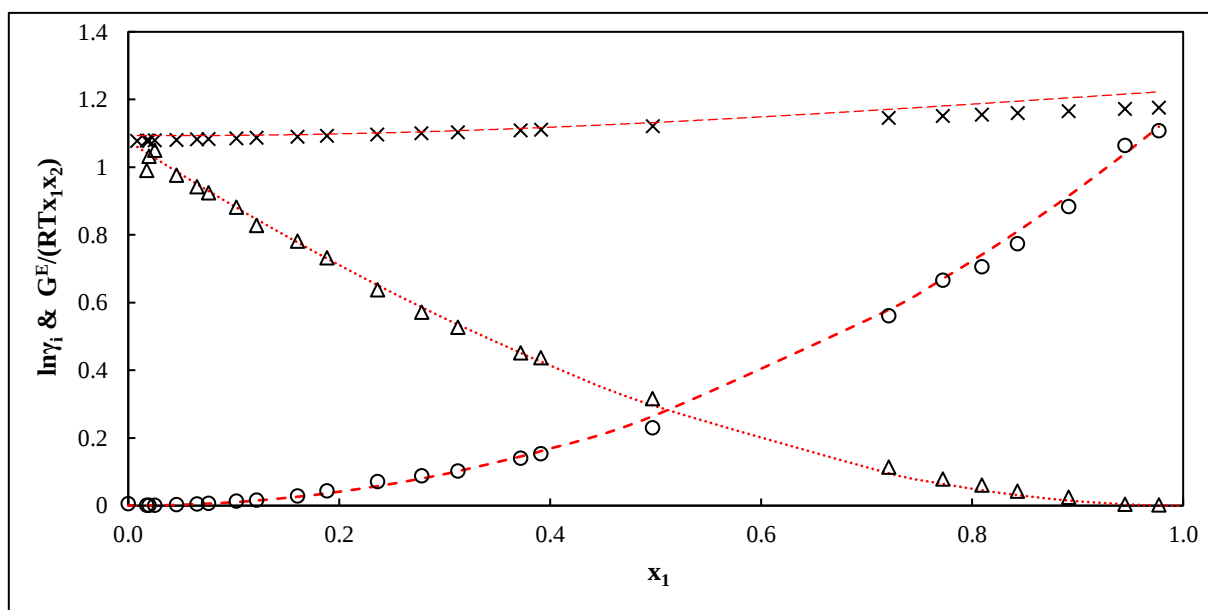


Figure E-4. Plot of $\ln\gamma_i$ ($\ln\gamma_1$ - Δ , $\ln\gamma_2$ - $\circ$) & $G^E/(RTx_1x_2)$ ($\times$) for the n-hexane (1) + pentan-2-one (2) system at 323.3 K using the infinite dilution test of (Kojima et al., 1990) and the UNQUAC-HOC model ($\ln\gamma_1$ - $\cdots$, $\ln\gamma_2$ - $---$, $G^E/(RTx_1x_2)$ - $-\cdot-$).

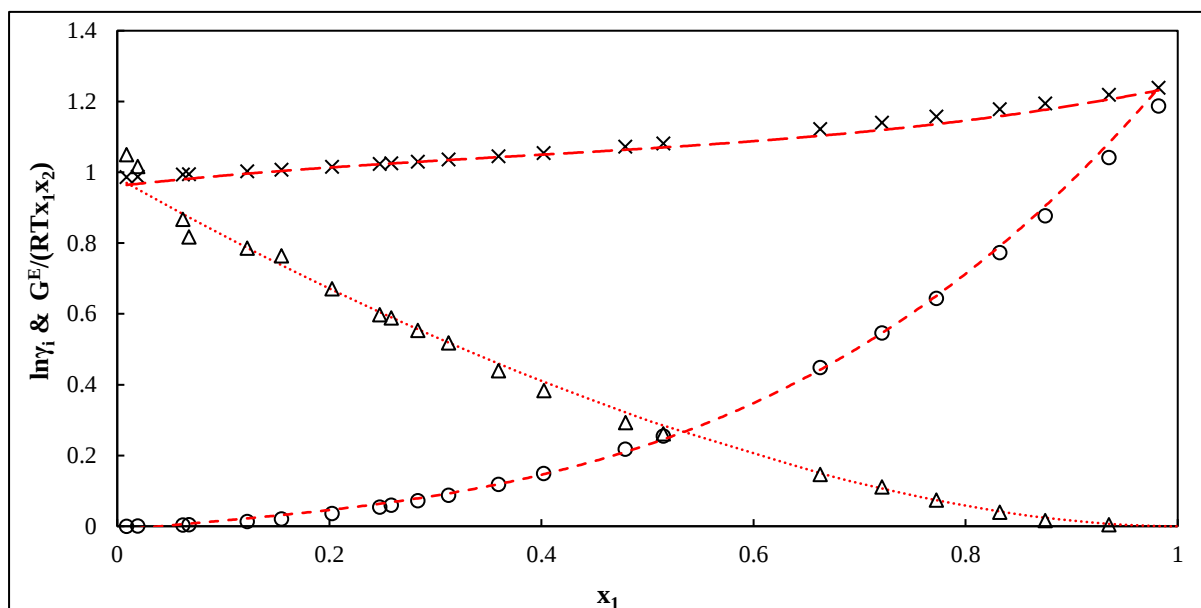


Figure E-5. Plot of $\ln\gamma_i$ ($\ln\gamma_1$ - Δ , $\ln\gamma_2$ - $\circ$) & $G^E/(RTx_1x_2)$ ($\times$) for the n-hexane (1) + pentan-2-one (2) system at 333.5 K using the infinite dilution test of (Kojima et al., 1990) and the UNQUAC-HOC model ($\ln\gamma_1$ - $\cdots$, $\ln\gamma_2$ - $-\cdot-$, $G^E/(RTx_1x_2)$ - $---$).

E2. n-hexane (1) + 4-methylpentan-2-one (2) VLE system

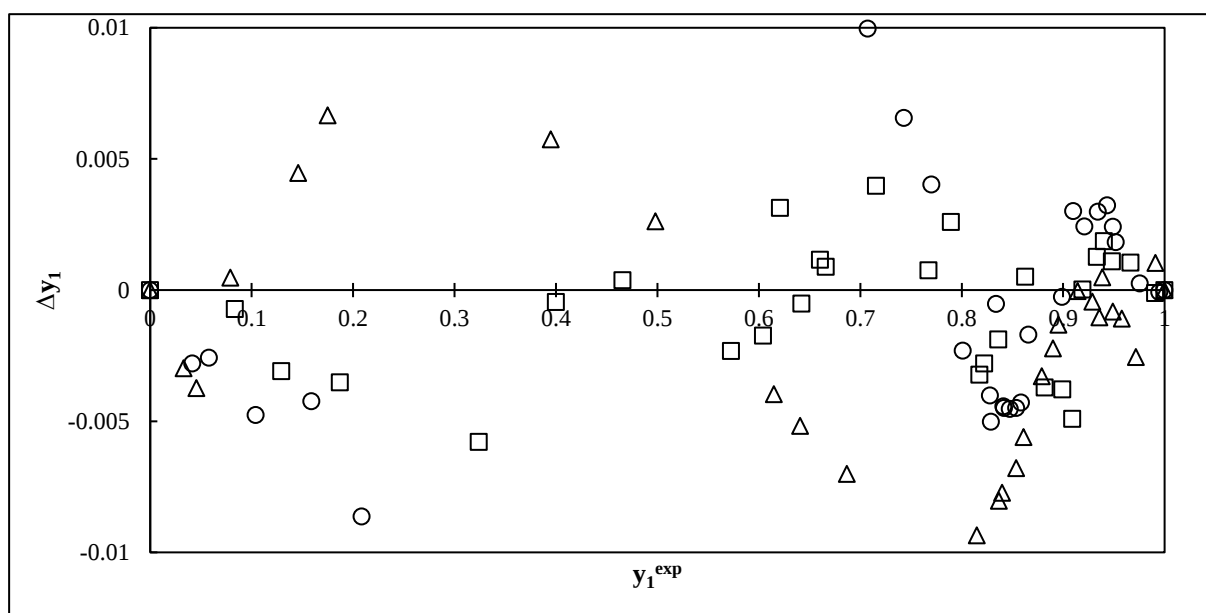


Figure E-6. Plot of deviations in y for the n-hexane (1) + 4-methyl-pentan-2-one (2) system at ($\circ$ -313.3, $\square$ -323.3 and Δ -333.6) K using the point test of (Christiansen and Fredenslund, 1975).

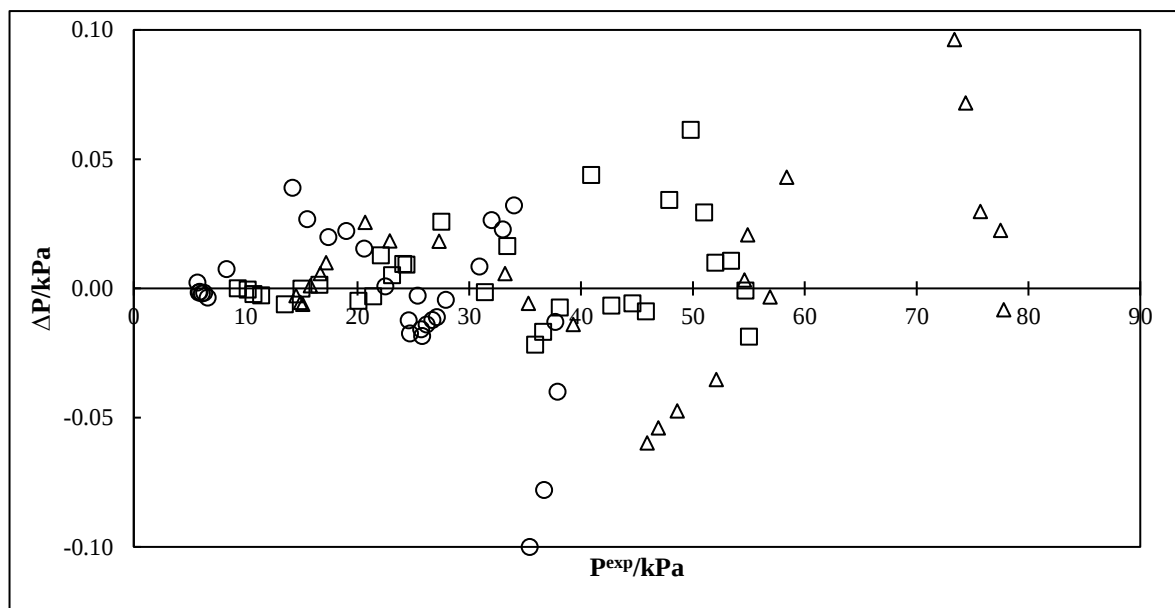


Figure E-7. Plot of deviations in P for the n-hexane (1) + 4-methyl-pentan-2-one (2) system at ($\circ$ -313.3, $\square$ -323.3 and Δ -333.6) K using the point test of (Christiansen and Fredenslund, 1975).

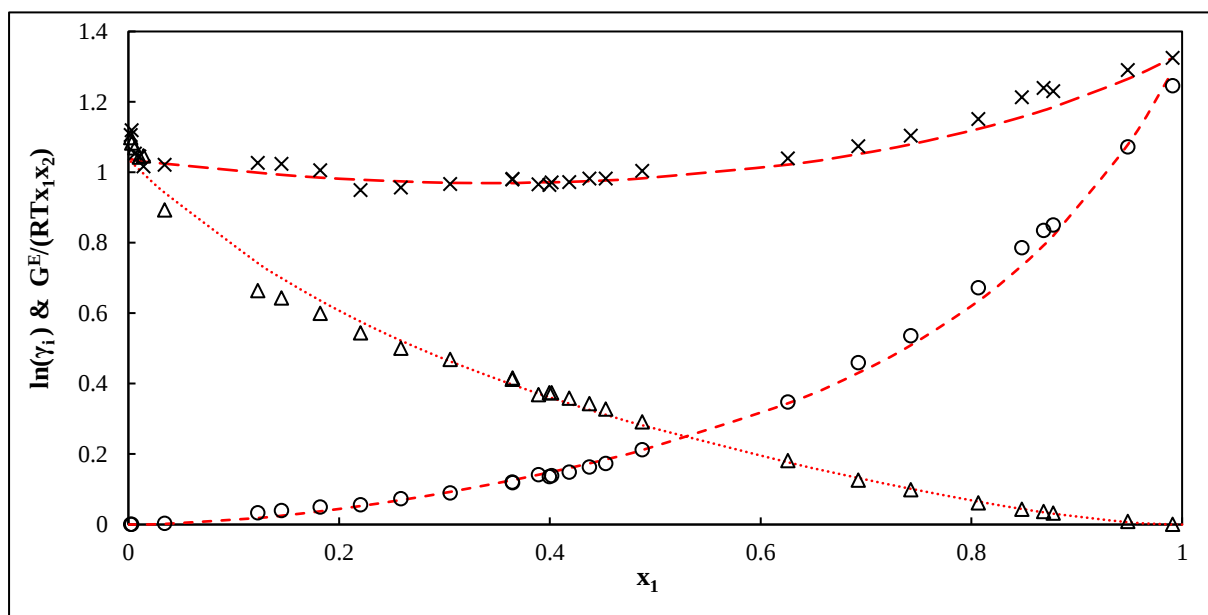


Figure E-8. Plot of $\ln\gamma_i$ ($\ln\gamma_1$ - Δ , $\ln\gamma_2$ - $\circ$) & $G^E/(RTx_1x_2)$ ($\times$) for the n-hexane (1) + 4-methylpentan-2-one (2) system at 313.3 K using the infinite dilution test of (Kojima et al., 1990) and the UNQUAC-HOC model ($\ln\gamma_1$ - $\cdots$, $\ln\gamma_2$ - $---$, $G^E/(RTx_1x_2)$ - $-.-$).

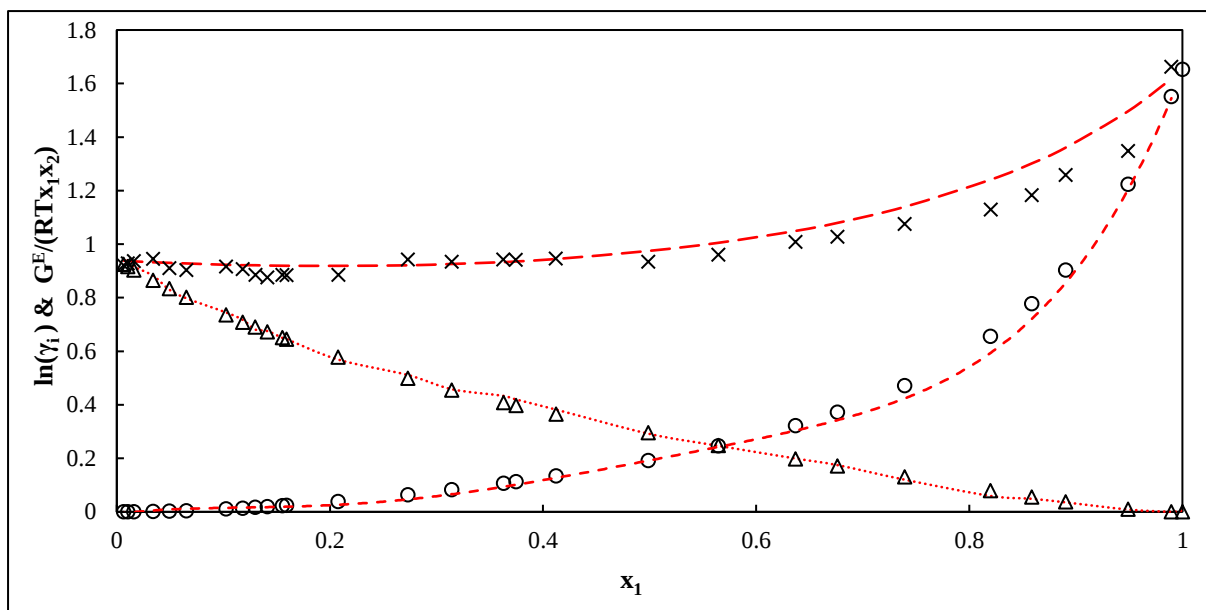


Figure E-9. Plot of $\ln\gamma_i$ ($\ln\gamma_1$ - Δ , $\ln\gamma_2$ - $\circ$) & $G^E/(RTx_1x_2)$ ($\times$) for the n-hexane (1) + 4-methylpentan-2-one (2) system at 323.3 K using the infinite dilution test of Kojima et al. (1990) and the UNQUAC-HOC model ($\ln\gamma_1$ - $\cdots$, $\ln\gamma_2$ - $-\cdot-$, $G^E/(RTx_1x_2)$ - $---$).

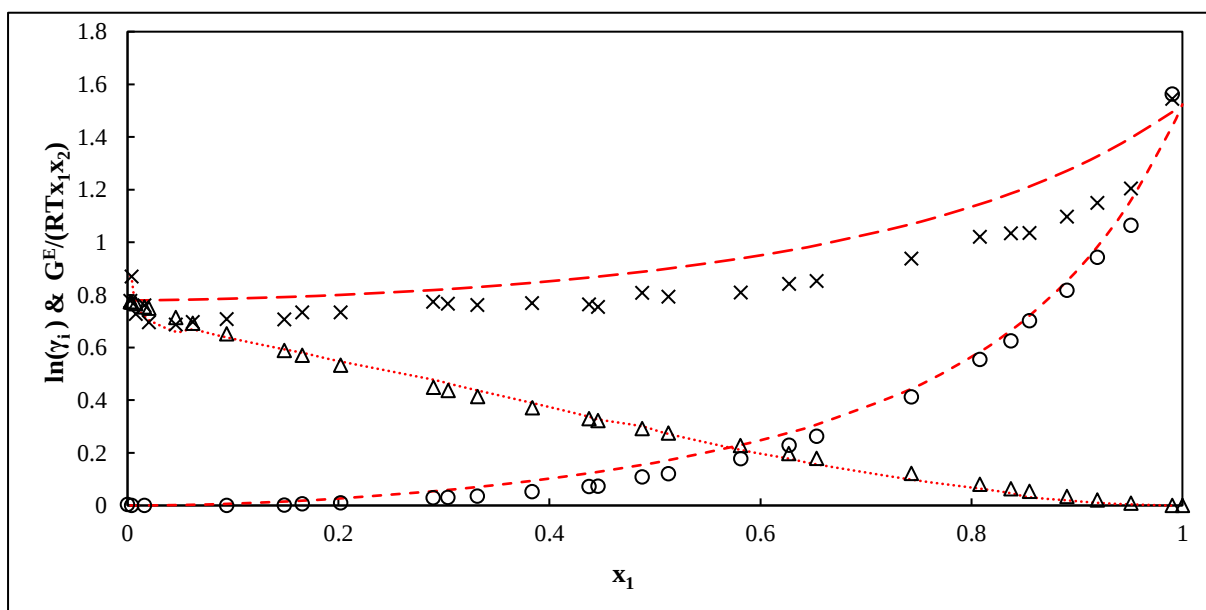


Figure E-10. Plot of $\ln\gamma_i$ ($\ln\gamma_1$ - Δ , $\ln\gamma_2$ - $\circ$) & $G^E/(RTx_1x_2)$ ($\times$) for the n-hexane (1) + 4-methylpentan-2-one (2) system at 333.6 K using the infinite dilution test of Kojima et al. (1990) and the UNQUAC-HOC model ($\ln\gamma_1$ - $\cdots$, $\ln\gamma_2$ - $-\cdot-$, $G^E/(RTx_1x_2)$ - $---$).

APPENDIX F

Blending Calculations

The following procedures are summarized from (Fahim et al., 2010). Product qualities are predicted through correlations that depend on the quantities and the properties of the blended components.

F.1: Blending mixing rule

The desired property P_{blend} of a blended product may be determined using the following blending rule (Fahim et al., 2010) :

$$P_{blend} = \frac{\sum_{i=1}^n q_i P_i}{\sum_{i=1}^n q_i} \quad (F-1)$$

Where P_i is the value of the property of component i and q_i is the mass volume or molar flowrate of component i contributing to the total amount of the finished product q_i can be volume fraction x_{vi} , therefore the denominator will equal to 1.

The blending mixing rule in equation F-1 assumes that the given property is linear (additive). Properties such as specific gravity, boiling point and sulphur content are additive. However, viscosity, flash temperature, pour point, Reid vapour pressure and cloud point are usually not additive.

F.2: Reid Vapour Pressure (RVP) Blending

RVP is the Reid vapour pressure at 100°F of a product determined in a volume of air four times the liquid volume. RVP blending indices are typically used in blending calculations since RVP is not an additive property.

The Chevron Oil Trading Company developed a commonly used RVP index based on the empirical method:

$$BI_{RVPi} = RVP_i^{1.25} \quad (F-2)$$

Where, BI_{RVPi} is the blending index of component i , and RVP_i is the RVP of component i in psi.

Using the index, the RVP of a blend is estimated as:

$$BI_{RVP,Blend} = \sum_{i=1}^n x_{vi} BI_{RVPi} \quad (F-3)$$

Where x_{vi} is the volume fraction of component i .

F.3: Octane Number Blending

Octane numbers are blended on a volumetric basis using the blending octane numbers of the components (Fahim *et al.*, 2010). Generally, octane numbers have a non-linear blending profile, hence adjusted blending octane numbers are used to calculate true octane number of a blend. These blending octane numbers are generally calculated by empirical correlations:

$$(True\ octane\ Number\ of\ a\ blend)\ ON = \sum x_{vi} \times ON_i \quad (F-4)$$

Where x_{vi} is the volume fraction of component i in the blend, and ON_i is the blending octane number of component i