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Vapour-Liquid Equilibrium of by-Products n-Alcohols and 1,3-Propanediol from Polyol Production

by

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Abstract

A new method for collecting vapour-liquid equilibrium data for binary mixtures is proposed in this work. A modified differential scanning calorimetry technique was used by evaluating the sample temperature instead of the heat flow. This method was tested on three well known systems and the results from this technique agreed very well with published data.

This new method was then used for determining the vapour-liquid equilibrium behaviour of binary mixtures of 1-hexanol, 1-heptanol, 1-nonanol and 1,3-propanediol. Correlation of the experimental data was done using both activity coefficient and equation of state models. An azeotrope was found in the 1-nonanol and 1,3-propanediol binary system but not for the other binary pairs. Therefore, an alternative for conventional distillation should be considered in order to separate these two main components.

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Table of Contents

List of Figures

List of Tables

List of Symbols

ABBREVIATIONS

ASTM	American Society for Testing and Materials
CAS	Chemical Abstracts Service
EOS	Equation of State
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTA	Differential Temperature Analysis
GD	Gibbs Duhem
HP DSC	High Pressure Differential Scanning Calorimetry
MT DSC	Modulated Temperature Differential Scanning Calorimetry
NRTL	Non-Random Two-Liquid
OF	Objective Function
PR	Peng Robinson
PRSV	Peng Robinson Stryjek Vera
RK	Redlich Kwong
SiC	Silicon Carbid (Carborundum)
SRK	Soave Redlich Kwong
TA	Thermal Analysis
TG	Thermo Gravimetry
vdW	van der Waals
vL	van Laar
VLE	Vapour Liquid Equilibrium
VLLE	Vapour Liquid Liquid Equilibrium

SYMBOLS

A_{ij}	Activity Coefficient Parameter
a	Force Parameter of an equation of state
b	Volumetric Parameter of an equation of state
c	Volumetric Parameter of an equation of state
F	Degree of Freedom
K	Distribution Coefficient
k_{ij}	Binary Interaction Parameter of an equation of state
N	Number of Components
P	System/Phase Pressure (mmHg, kPa)
P_c	Critical Pressure (Pa, kPa)
P_r	Reduced Pressure (Pa, kPa)
t	Time (s, min)
T	System/Phase Temperature (°C)
T_c	Critical Temperature (K)
T_r	Reduced Temperature (K)
V	System/Phase Volume (m^3, mL, L)
V_i	Wilson Volumetric Parameter
x	Liquid Mole Fraction
y	Vapour Mole Fraction
$\overline{\Delta P}$	Pressure Mean Deviation (mmHg, kPa)
$\overline{\Delta y}$	Vapour Mole Fraction Mean Deviation

GREEK SYMBOLS

α	Third Parameter of NRTL Model
γ	Activity Coefficient Parameter
κ	Experimental Parameter of PR EOS
π	Number of Phases
φ	Fugacity Coefficient
ω	Acentric Factor

SUBSCRIPTS

1	Lighter component in a binary
2	Heavier component in a binary
12	Interaction between components in a binary
c	Critical
i	Component
r	Reduced

SUPERSCRIPTS

L	Liquid
sat	Saturated
V	Vapour

1. Introduction

Polyurethanes are mostly produced from petrochemicals and according to the depletion and increasing cost of oil, the interest to find an alternative method is rising [1-3]. Using vegetable oils is an environmental friendly and renewable source for manufacturing polyols. Therefore, canola oil has been used to produce polyurethanes [4] in a two-step chemical reaction. A polyol monomer aimed to be used in bioplastics (polyurethanes) is the result of this reaction. This reaction sequence consists of ozonolysis and hydrogenation. First, the carbon-carbon double bonds of the fatty acids of the oils (e.g. canola, flax), which are triglycerides, are cleaved through the ozonolysis step. Then, through hydrogenation a series of alcohols are produced [4]. These alcohols are of interest to be separated and marketed to the chemical industry. The final result of this two-step reaction includes a triglyceride polyol and other alcohols such as 1-nonanol, 1,3-propanediol (PDO), 1-hexanol and very small amount of 1-heptanol. The linear alcohols are the result of unsaturated fatty acids chains (i.e. oleic, linoleic and linolenic) fracturing.

The produced alcohols after the hydrogenation step are considered as raw materials for manufacturing various useful industrial chemicals. Pure 1-hexanol is abundantly available. As PDO is a low molecular weight diol, its applications are mainly in manufacturing polyesters, polyurethanes, composites, plasticizers, adhesives, personal care products, detergents, coatings and paints. Therefore, a biobased production method of all of these alcohols is highly of interest to industry.

Determining suitable separation sequence(s) to separate the by-product alcohols is the long-term objective of this project. As stated, the alcohol based mixture mainly contains 1-nonanol, 1,3-propanediol, 1-hexanol and very small amount of 1-heptanol. From the viability point of view, each alcohol needs to be separated and purified to 98 weight %. In order to determine and design the appropriate separation process, vapour liquid equilibrium data of each mixture consisting of the by-product alcohols first needs to be determined. By the reason of similarity of boiling temperatures of 1-nonanol and 1,3-propanediol, the most challenging aspect of this project is to determine vapour liquid equilibrium of this mixture.

Many different techniques [5-7] for determining vapour liquid equilibrium of mixtures are discussed in Chapter 2. In this project, the aim is to determine vapour liquid equilibrium data of six different binary mixtures. A new technique for determining these data will be used. In this study, differential scanning calorimetry (DSC) will be used. It is a thermal analysis instrument in which both the sample pan and the reference pan, which is deliberately chosen to be empty, undergo a heating/cooling procedure with a same heating/cooling program. The idea is to compare the discrepancies between the measured heat flows of sample and reference and then report it as a thermogram signal [8]. However, analyzing sample temperature, discrepancy between sample and reference temperatures and their first and second derivatives are studied in this project in order to determine boiling point(s) of mixtures with different compositions. The concept of using Differential scanning calorimeter is discussed in detail in Chapter 3.

The primary goal of this study is to assess the accuracy and validity of using a differential scanning calorimeter to determine vapour liquid equilibrium data of binary mixtures. This approach is explained in Chapter 4 by benchmarking the collected data for pure water as well as methanol/water, isopropanol/water and cyclohexane/toluene systems against published data [9-14]. If an agreement with the authentic published data for all of mentioned systems and pure water is observed there would be interest to use this technique for determining vapour liquid equilibrium data of new mixtures. It is notable that thermodynamic modeling and correlation will also be done for fitting equilibrium data with the experimental ones using different activity coefficient models.

The results for new binary mixtures are discussed in Chapter 5. As indicated, determination as well as design of a proper separation sequence is based on the equilibrium data. Whether a binary mixture contains an azeotrope or not is one of the best factors that determine which separation process can be used for that mixture. Concerning data correlation and fitting, the collected experimental data i.e. T-x curves are first correlated and fitted using activity coefficient models, that is, an activity coefficient model is chosen as the best fit based on the mean deviation of temperature. Then, Peng-Robinson equation of state combined with Margules and van Laar mixing rules will be used to model and correlate experimental data as a whole.

2. Vapour Liquid Equilibrium

2.1 Nature of Equilibrium

When the macroscopic properties of a system such as phase compositions, temperature and pressure undergo no changes, the system is said to be at equilibrium. In contrast, from the microscopic point of view, the system is dynamic and the properties are changing. However, a balance of all potentials that may bring about changes in the properties of the system always exists [15]. A tendency for changes originates from a difference in potential as the difference in levels cause the water to flow between two containers. In the case of water, the level affects the potential energy of the water in the containers. Similarly, when a chemical potential difference exists between two parts of a container or equipment, a chemical stream flows. Customarily, when a liquid is being heated, the vapour pressure of the liquid increases until it reaches the exerted pressure from the surroundings, and then it remains at a constant temperature and pressure during boiling. The liquid is in equilibrium with its vapour during the boiling event.

2.2 Phase Equilibrium

An isolated system, consisting of multiple phases in contact, ultimately accomplishes a state in which no alternations takes place and the temperature, pressure, and phase compositions remain constant. Also, the temperature and pressure of all phases are equal. As stated, at microscopic scale, the conditions are not static but dynamic.

2.2.1 Phase Rule

In order to characterize the state of equilibrium, some variables must be determined or measured. The number of these independent variables is exactly the difference between the total number of intensive variables and the independent equations which can be considered to link the intensive variables [15]. For studying a system in equilibrium which contains N chemical species and π phases, the temperature T, pressure P, and all mole fractions must be determined. Thus, $2 + N\pi - \pi$ variables including T, P, and $(N - 1)$ mole fractions of each phases must be determined. Regarding the equations, for each specimen $(\pi - 1)$ phase equilibrium equations can be written. Consequently, the degrees of freedom of the system F can be calculated as below, which is known as the phase rule [15]:

$$F = 2 - \pi + N \qquad \{1.1\}$$

2.2.2 Duhem's Theorem

In the case of a closed system, π extensive variables i.e. the mass or mole fraction of all phases should be determined. Therefore, $N\pi$ mass balance equations also can be written. Equation {1.1} can be reorganized to the following format known as Duhem's phase rule theorem [15]:

$$2 + N\pi - \pi + \pi - N\pi = 2 \qquad \{1.2\}$$

It is notable that the two independent variables may be either intensive or extensive. However, the number of intensive variables is given by Equation {1.1}, so when $F = 1$, at least one of the two variables must be extensive, and when $F = 0$, both variables must be extensive.

2.2.3 Vapour-Liquid Equilibrium

The coexistence of vapour and liquid at equilibrium is one type of several distinct types of phase equilibrium. If there is only one liquid phase as well as a vapour phase, then it is called vapour liquid equilibrium (VLE). Alternatively, if there are two liquid phases and one vapour phase present, then the system is a vapour liquid liquid equilibrium (VLLE). Based on the number of species, the mixture is called binary, ternary, quaternary, etc.

In the case of a binary system, $N = 2$, for VLE systems the degree of freedom, F, is equal to 2. Therefore, for ascertaining VLE data of each binary mixture, determining two intensive parameters at equilibrium is sufficient. These two variables can be both the temperature and pressure or both phase compositions. In binary systems, the more volatile compound is always called the “lighter” component and its boiling temperature is lower than the other component. Figure 1 shows an ordinary *T-xy* diagram for a binary mixture. Point *C* is attributed to the boiling temperature of the heavier compound, while point *D* is attributed to the boiling temperature of the more volatile compound. The surface area limited between *CAD* and *CBD* curves is the two phase area in which both vapour and liquid phases coexist. The area above the *CBD* curve is associated to vapour phase and the area below the *CAD* curve is of liquid phase. The *P-xy* diagram is analogous to a *T-xy* diagram, but the upper part would be associated to liquid and the lower part to vapour.

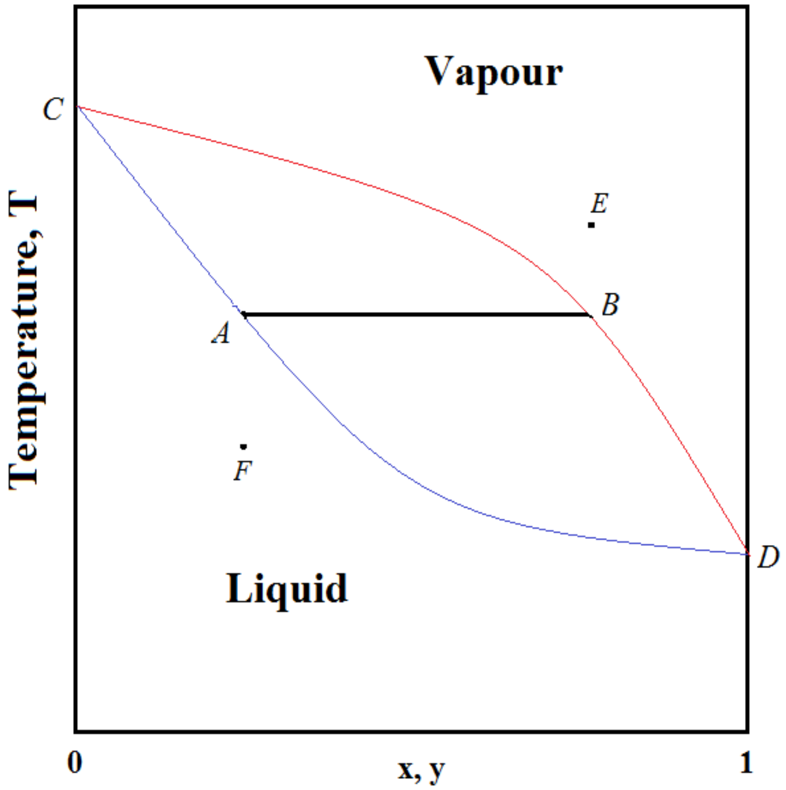

Figure 2-1: Sample *T-xy* diagram of a given binary mixture at constant pressure

2.2.3.1 Dew Point

In Figure 2-1, the *CBD* curve, which is the interface between two regions, is called dew point curve. Lowering the temperature of a known composition gaseous mixture i.e. the composition at point *E*, the mixture would be gaseous until it reaches this curve, *CBD*. At point *B*, the very first droplet of the liquid is formed and there would be two phases. The composition of the vapour is supposed to be the same as the initial compositions so that a small droplet of liquid cannot change the vapour phase composition. The composition of the liquid phase can be determined by continuing the isotherm *AB* line until it intersects the *CAD* curve and that composition is the composition point *A*. Point *B* is then called the dew point of that mixture.

2.2.3.2 Bubble Point

The *CAD* curve in Figure 2-1 illustrates the bubble curve. Similarly, if a known liquid mixture i.e. point *F* undergoes a heating process, when it reaches the *CAD* curve the very first bubble of the vapour is produced. The composition of the vapour is the composition of point *B* and the composition of the liquid is supposed to remain the same as initial composition.

2.2.3.3 Critical Point

The critical point for a pure species is the highest temperature and pressure at which both vapour and liquid phase can coexist. The same definition can be applied to a mixture. In case of binaries, the critical curve is the locus of the points at which both phases in equilibrium become identical. Therefore, this locus includes the critical points of various composition mixtures in the entire range, between 0 and 1.

Figure 2-2 shows the saturation lines in the vicinity of the critical point for a pure component. As shown in Figure 2-2, for a known composition binary mixture, the critical point, point *C*, is the point at which the saturated liquid and vapour meet each other in the *PT* diagram. However, for any point between *C* and *N*, which is the point at maximum temperature, if the pressure reduces the liquefaction occurs because it lies on the saturated vapour curve. This phenomenon is called retrograde condensation and the mentioned region in Figure 2-2 is the retrogration region. This phenomenon is important in the operation of deep natural gas wells where the pressure and temperature are in the mentioned region, so significant separation of the less volatile component is accomplished along the streamline from the wellhead [15].

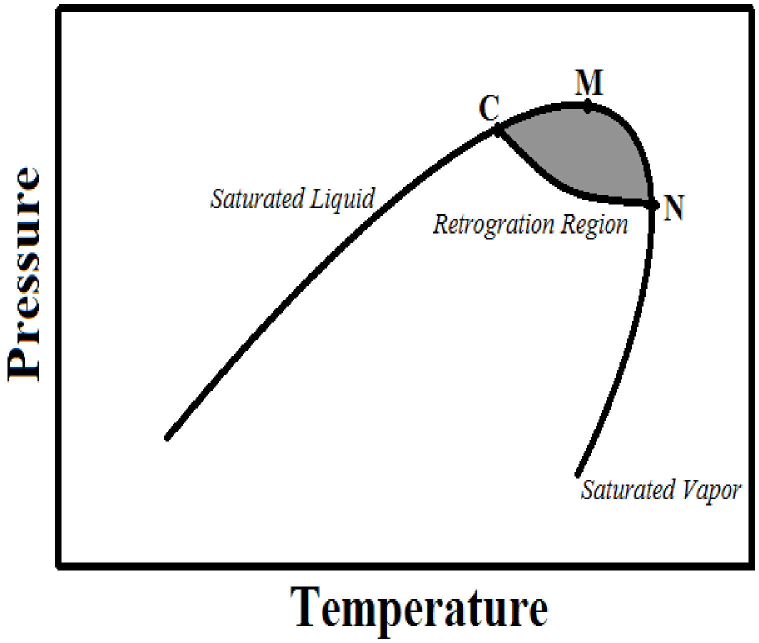

Figure 2-2: Retrogration condensation region of a binary mixture

2.2.3.4 Azeotrope

An azeotrope is a point at which the liquid and vapour compositions of each component in the mixture are equal. That is why a mixture containing an azeotrope is also called a constant boiling mixture. If an azeotrope is present in a mixture, the *P*-*xy* or *T*-*xy* diagram contains a minimum or maximum point(s) which are the azeotrope(s). It is impossible for an azetropic mixture to be separated by conventional distillation beyond the concentration at the azeotrope point.

2.2.4 Isothermal and Isobaric Equilibrium

In determining VLE data it is usual to maintain a constant temperature or pressure of the mixture in order to obtain more consistent results. Choosing which methodology to use depends on the application of the data, instrumentation, and analyzing method. Typically, isobaric data are preferable for industrial purposes as maintaining the pressure at a constant value during operation is easier and more economical. However, more isothermal data can be found in the literature because it is generally easier to gather data in such a manner. Also, the analyzing procedure is faster for isothermal data because the temperature and temperature dependent parameters are always implicit in the thermodynamic models.

2.2.5 Importance and Applications of VLE Data

Phase equilibria data in general and vapour liquid equilibria data in particular are considered very important data for the design and optimization of various unit operations. In chemical engineering, the basis for separation and/or purification processes relies on accurate vapour liquid equilibrium data [16]. As the world`s energy and raw materials are depleting, the demand of more efficient and accurate design of chemical processes increases. Therefore, when designing a separation process, highly accurate VLE data is needed to determine the number of equilibrium stages and size of the equipment and estimate the time to reach equilibrium. Hence, phase equilibrium data plays a significant role in design of the chemical processes and can be used to predict the behaviour of the involved chemicals in the processes in different conditions. Therefore, there is always a great demand for highly accurate thermodynamic data. Though large quantities of data have been collected, there is and will be more data needed to satisfy the needs of upcoming engineering problems. This data can also be used in order to improve and/or reconfirm practicality of the existing empirical equations, which are being used to design industrial or scientific equipment. This is done by adjusting binary interaction parameters correlated from VLE data [17].

Various types of VLE data including bubble point temperature or pressure i.e. Tx or Px, dew point temperature or pressure i.e. Ty or Py, flash i.e. PTz, and PTx, PTy, and $PTxy$ data have been used by both scientists and chemical engineers based on the specifications of the system as well as the scope and requirements of the project, and the applications of the data.

From the thermodynamic point of view, even though the laws of thermodynamics are indisputable, there is no definite knowledge of interactions among different molecules in a mixture that can predict the properties of the mixture based on the properties of each individual component, nor are thermodynamic laws able to predict the behaviour of a chemical accurately from its molecular structure. Hence, experimental data is needed to help engineers optimize their calculations and predictions. Usually thermodynamic data collection is highly time consuming and expensive, and then based on molecular thermodynamic models, the collected data is extrapolated where there is no data available [16]. Consequently, after collection of the experimental VLE data, modeling and correlating can be applied in order for the data to become useful. Different thermodynamic models have been tried which will be discussed further.

2.3 Methods of Determining VLE data

In general, these are three methods for measuring VLE data; static; dynamic and dew-and-bubble point [5-7]. Each method demands different designs, instrumentations, and conditions. As stated earlier, the method is usually chosen based on the application of the VLE data.

2.3.1 Static Methods

In static methods, the liquid mixture is in a closed and evacuated cell and will remain until it reaches equilibrium at the given temperature. Then, the pressure, temperature, and volume are measured. The liquid composition is determined from the amount of transferred liquid to the cell. Due to slight vapourization of liquid, a correction is needed to be applied. The vapour phase data is not measured in this method, however, it is inferred and calculated from the measured *PTx* data by means of integration of the Gibbs-Duhem equation [18]. Syaegh and Vera [19] suggested not involving the analysis of liquid phase compositions in order to reduce the amount of errors associated with the liquid volume determination. Therefore, the temperature and pressure were the only parameters being measured at equilibrium. The liquid compositions were calculated from the material balance based on the known overall initial composition.

Advantage of using static method is to completely avoid experimental difficulties in measuring vapour phase compositions [20]. However, no actual thermodynamic consistency test can be applied to the experimental results without measuring the vapour phase compositions [17]. This method is commonly used to attain isothermal data. Furthermore, all liquid feeds must be degassed before being analyzed. Nevertheless, the effect of degassing is inevitable and often hard to be detected. Mentzer *et al.* [5] discussed the measurement techniques based on static methods comprehensively.

2.3.2 Dynamic Methods

The dynamic method is also called circulation method because of the circulation of the phases in the VLE device. The principle of circulation methods is a steady state under which continuous separation of vapour phase from the liquid phase occurs and the vapour stream re-circulates back to the liquid phase and eventually the thermodynamic parameters such as the temperature and pressure equilibrate [6]. The earliest recirculation still was used by Carveth in 1899 [21] and modified by Sameshima in 1909 [22]. According to the number of recirculated streams and thermodynamic conditions, recirculating stills are classified in three groups [6]. These types of equilibrium devices can be used either for constant pressure or constant temperature.

2.3.2.1 Condensate Recirculation Methods

In this method, the vapour leaving the equilibrium chamber is condensed and the required pressure differential is compensated by the hydrostatic head of the condensed vapour [6]. Circulation continues until equilibrium and then the temperature, pressure, and the composition of phase(s) are measured. According to operational forms, the method can be classified in two sub-groups.

2.3.2.1.1 Liquid condensation recirculation

In this type, the condensate vapour re-enters the equilibrium chamber as liquid and the circulation takes place. Carveth [21] proposed a design for VLE data collection based on the principle of recirculation of the condensate vapour and his still cell has been modified and improved and became very popular because of its simple design and ease of use. However, requiring a long time to reach equilibrium, partial condensation of vapour, inaccurate determination of the equilibrium temperature and impossibility of attaining uniform composition of liquid phase limits the accuracy of these recirculation cells. The low accuracy of this type has also been observed by applying thermodynamic consistency tests to the obtained VLE results [6].

2.3.2.1.2 Re-vapourized Condensate Methods

Re-vapourization of the condensate vapour in a heater is the principle of this type of cells. It was first proposed and developed by Chilton [23] in 1935 and it has been improved because of its highly accurate VLE data. The main difficulty of this method is the balancing of heat losses in the residue chamber. Low accuracy of the pressure and temperature measurement owing to pressure drop led from bubbling of the vapour through the liquid and time consuming operational procedure are the other potential drawbacks of this method.

2.3.2.2 Vapour Recirculation Methods

Inglis [24] first proposed the vapour recirculation method in 1906. In this method, the vapour is being re-circulated by a pump which sends the vapour through the standing liquid by means of a heat interchange system e.g. thermostat until steady state is achieved [6]. Then, the compositions, pressure and temperature are measured. Even though this technique is simple to use, it still has limitations such as: pressure fluctuation; liquid entrainment in the vapour stream; condensation of vapour and difficult vapour sampling at low pressures. A very comprehensive and detailed study on this type of cells was done by Tsiklis [25] in 1968 which describes all modification which have been applied in order to overcome those mentioned problems.

2.3.2.3 Liquid and Vapour Condensate Recirculation Methods

The most broadly used method among all recirculation methods is the method based on the recirculation of both the liquid and condensate vapour. This concept was first proposed by Cottrell [26] in 1901 while he was trying to use the cell for determining boiling points. Chronologically, the apparatus was significantly improved by Washburn [27], Swietoslawski and Romer [28], Swietoslawski [29], and Gillespie [30]. A review of numerous types of this method was done by Hala *et al.* [18]. In this type of still, both the liquid and condensate vapour are separated and re-circulated. The measured temperature of the mixture and the liquid phase composition using a Cottrell pump are closest to the relative measured thermodynamic data at true equilibrium. Therefore, simultaneous recirculation of vapour and liquid generates more accurate VLE data among other types of dynamic cells in which only one phase is circulated.

2.3.3 Dew and Bubble Point Methods

The dew and bubble point method is practicable for binary mixtures only. The advantage of this method is eliminating sampling and analysis of both vapour and liquid phases. The method can be used either for isothermal and isobaric methods. If the temperature is constant, the pressure is interpolated from the temperature-volume *TV* curve, and in case of an isobar experiment, the temperature can be derived from the pressure-volume *PV* curve. As such, the accuracy of the technique is restricted by graphical and/or numerical interpolation method [7]. Determination of the bubble and dew points rely on the appearance of small bubbles and opalescence appearance of liquid droplets, respectively. The earliest use of this technique came back to 1877 while Cailletet [22] was studying liquefaction of acetylene. The first use of the technique for mixtures was done by Kuenen [32] in 1895 as he used a known composition of a gaseous binary mixture and introduced it to a capillary tube and then measured the dew point of the mixture. The technique is commonly used as isochoric still equilibrium cells [7]. However, Sage *et al.* [33] designed a variable-volume cell in which the volume of the mixture was controlled by adding or withdrawing exact amounts of mercury. The most important note of using this technique is degassing the sample inasmuch as the presence of non-condensable gases results in serious errors. The degassing is much more essential when investigations are done at pressures below atmospheric. The advantages of using this technique are eliminating sampling and separate analysis of each phase and measuring molar volume of each phase as well as total pressure data. However, this technique is valid only for the thermodynamic conditions below the critical point of any system [7]. Although this method is preferable for binary mixtures only, it has been extended to multi component systems [34, 35]. Dew and bubble point method can be used for both isothermal and isobaric conditions.

A comparative study of a static still and a liquid and vapour condensate recirculation cell by Malanowski [36] demonstrated that according to thermodynamic consistency tests, the results of dynamic cell were more reliable. The other advantages of vapour and liquid recirculation cells in comparison to static cells are ability to collect both isothermal and isobaric data, no need for degassing liquid, faster VLE data collection, and wider pressure range. Therefore, the liquid and vapour condensate recirculation stills are the most common used and popular equipments for obtaining VLE data.

2.4 Thermodynamic Modeling

In order to use VLE data to simulate separation processes, they need to be modeled and correlated. Hence, thermodynamic models must be applied to the experimental data in order to correlate them. Also, thermodynamic consistency tests should be applied to the obtained data in order to examine the accuracy and consistency of the experimental results. Customarily, these tests are based on the chosen thermodynamic models. As Ammar and Renon [37] stated equations of state (EOS) and activity coefficient models are the thermodynamic means to analyze experimental VLE data. Today, computer programming is a faster way to use a thermodynamic model and the most challenging part would be minimizing the operation time and errors. The biggest issue in using these models, which sometimes are misused, is being aware of the range where they were derived originally. Due to the empiricism of these models, it is not advisable to go beyond their range by extrapolation. Hence, it is critical to check the accuracy and consistency of these models in the extrapolated ranged in order to find the limitation of their application, necessary correlation for other ranges, and improvement and development for further use.

2.4.1 Equations of State

Equations of state, (EOS) models are also known as K-value methods in which *K* is defined as the ratio of the composition of each substance in the vapour phase to its composition in liquid phase. Equations of state methods are actually numerical methods for solving nonlinear phase equilibrium equations derived from the equality of chemical potential of every component in all phases and the overall mass balance. Equation {1.3} defines the equality of fugacities in both phases [15].

$$(x\varphi^{L})_{i} = (y\varphi^{V})_{i} \ldots\ldots\ldots\ldots \{1.3\}$$

Where, x and y are the liquid and vapour phase compositions, respectively, and φ is the fugacity coefficient of each component. Subscript i stands for the component and superscripts L and V are associated to liquid and vapour phase correspondingly. Parameter φ is calculated from an EOS; therefore, in determining phase equilibrium there is a need for an EOS.

There are a large amount of published equations of state with different levels of complexity, e.g. they can have a range from one to four adjustable parameters. Complicated equations such as those offered by Chapman *et al.* [38] and Strobridge [39] are more applicable when very accurate *PVT* data is needed. However, simpler equations such as those of Redlich-Kwong [40], Soave-Redlich-Kwong [41], Peng-Robinson [42], and Peng-Robinson-Stryjek-Vera [43], are accurate enough when the phase equilibrium i.e. VLE calculation is needed, especially when they are combined with specific mixing rules. Even though the nature of these models is semi-empirical, they can be used to predict the properties of both pure compounds and mixtures with high level of accuracy as long as they are used in the ranges in which the correlations were obtained. Based on the intermolecular interactions, there are three main types of equations of state.

2.4.1.1 Van der Waals-Type Equations of State

The first attempts for proposing an equation of state after Boyle in the 17th century were done by van der Waals (vdW), more than a century ago. He was able to represent *PVT* behaviour of fluids. Equation {2.4} is the basic cubic van der Waals equation of state (vdW EOS), which has been widely and largely modified so far [44].

$$P = RT / (V - b) - a / (V (V + d) + c (V - d)) \quad \text{.............} \; \{2.4\}$$

Parameters *a*, *b*, *c*, and d are generally functions of temperature and properties of pure fluids such as the acentric factor and normal boiling point. These parameters are usually determined by theoretical and empirical studies [45, 46]. Many more accurate equations of state have been developed and used after vdW for predicting *PVT* and vapour liquid equilibrium data. In some modifications, more attention has been paid to use more temperature dependency to earlier proposed equations of state. This type of equation of state is itself divided into two groups; cubic-empirical and non-cubic equations of state. The Redlich-Kwong (RK), Peng-Robinson (PR), and modified versions of these equations, Soave-Redlich-Kwong (SRK), and Peng-Robinson-Stryjek-Vera (PRSV) are the most popular cubic equations of state. The other group called non-cubic EOS includes Carnahan-Starling [47], BACK [48], Heiling-Franck [49], and Dieters [50]. All proposed van der Waals-type equations have been modified by several researchers and a very comprehensive review of this type of equations has been done by Sengers *et al.* [51].

2.4.1.2 Molecular Based Equations of State

Molecular based equations are another type of equations of state consisting of two groups; chain-molecules and associating fluids. Molecular based equations have become popular; however, there is some inaccuracy for predicting thermodynamic data by a single EOS even with many defined parameters. Several attempts have been made to review the power and usefulness of these types of equations of state as well as the cares which should be taken using molecular based equations [51-53]. Non empirical nature of these types of EOS sometimes results in unexpected errors as a disadvantage.

2.4.1.3 Virial-Type Equations of State

This type includes the modifications and expansions applied to Virial equation of state [15]. Beattie-Bridgeman [54], Benedict-Webb-Rubin [55] and its modifications like mBWR [56], BWR-Nishiumi [57-60], and BWR-Starling-Han [61] are some examples of the Virial-type equations of state. Anderko [62] has reviewed this type of equations of state in his publication.

2.4.2 Application of Equations of State to Mixtures

Predicting properties of a mixture is the next level in terms of complexity for an EOS. This requires more adjustable parameters which results in more deviation from ideality. In order to apply an EOS to a mixture, a mixing rule for temperature dependant parameters is expected. During the past 30 years, equations of state have been investigated in order to be used for systems consisting non-ideality, polarity, and association. Using multiple interaction parameters [63, 64], non-quadratic mixing rules and local-composition mixing rules [65] as well as combining excess Gibbs free energy models and EOS [66] are different concepts that have been examined in this period.

2.4.3 Mixing Rules

The mixing rule is used to rearrange the parameters which are dependent of the properties of each individual substance to a parameter which is a function of the properties of all involved species in the mixture. As such, an interaction parameter is usually considered when combining mixing rules with an EOS. The very first suggested mixing rule was accredited to van der Waals and defined in the format which considers geometric mean for the force parameter, a, and arithmetic mean for the volume parameters, b and c. Afterwards, the concept of using concentration-independent interaction parameters has been developed. However, even using these modifications the model still did not work in some complicated cases like supercritical fluids [44].

Considering concentration-independent interaction parameters concept needs some optimization programs to help the parameters to be determined. Customarily there is an objective function (OF) which consists of summation of one or more difference values of experimental and calculated values. In order to find the values of interaction parameters, the goal is to minimize the defined OF. Obviously, the results would be a function of OF, tolerance value, and precision. Several mixing rules have been proposed, modified, and used in order to predict PVT behaviour of the mixtures. Solorzano *et al.* [67] presented a comparative study of various mixing rules, but for cubic equations of state predicting VLE data of mixtures.

As of this end, using equations of state is a means to predict PVT behaviour of compounds and mixtures. Extending the use of equations of state to mixtures requires a mixing rule which tries to model the parameters of the mixture like a pure compound. The most appropriate

EOS for each compound and/or mixture depends on the nature of the involved chemicals. Polarity, polymeric, symmetry, associability, and super criticality are the determining factors in the process of choosing a proper EOS as well as a mixing rule. For instance, a proper combination of an EOS and a mixing rule for a polar-nonpolar mixture might not be proper for a polar-polar mixture as well. Also, either symmetric or asymmetric mixtures need different equations. A review publication by Valderrama [44] recommended and generalized the most appropriate combination of equations of state and mixing rules for different types of vapour liquid mixtures. However, there is no unique equation that can be used to predict all properties of any component regardless of the properties of the component itself and the temperature and pressure range. Therefore, care should be taken while choosing and using equations of state and mixing rules.

Among all cubic equations of state, SRK and PR equations of state are the most two popular equations of state because of their capability and simplicity in predicting PVT and other thermodynamic data with high accuracy. One of the major contributions was made by Stryjek and Vera to modify the PR EOS. The following equations describe the PR EOS [15]:

$$P = \frac{RT}{V-b} - \frac{am(Tr,\omega)}{V(V+b)+b(V-b)} \text{..................................} \{2.5\}$$

$$a = 0.45724\ RT_c^2 / P_c \text{....................................} \{2.5\ a\}$$

$$b = 0.07780\ RT_c / P_c \text{....................................} \{2.5\ b\}$$

$$m = [1 + \kappa\ (1-T_r^{0.5})]^2 \text{...................................} \{2.5\ c\}$$

In Equation {2.5 c} the parameter κ is a parameter which is a function of acentric factor only and is described asbelow:

$$\kappa = 0.37464 - 1.54226\omega - 0.26992\omega^2 \text{.....................} \{2.6\}$$

In the above equations, R is gas global constant, T_c and P_c are critical temperature and pressure, and ω is acentric factor. Stryjek-Vera's made a modification to the original PR EOS. That is, they add another parameter to the equation itself which its nature is empirical and is calculated from vapour pressure data of the pure component. Equations {2.7} and {2.7 a} give the modification proposed by Stryjek and Vera [43].

$$\kappa = \kappa_0 + \kappa_1 (1 + T_r^{0.5}) (0.7 - T_r) \text{..........................} \quad \{2.7\}$$

$$\kappa_0 = 0.378893 + 1.4897153\ \omega - 0.17131848\ \omega^2 + 0.019655\ \omega^3 \text{.....} \{2.7\ a\}$$

The PR EOS itself is the modification for SRK in the volume dependency of the attractive pressure term i.e. the second term of each EOS. The results have been shown that this modification could result in obtaining better liquid volumes and better VLE calculations. Also, it is notable that SRK and RK are accurate enough for most gaseous mixtures [44].

2.4.4 Activity Coefficient Models

To justify a deviation from ideal behaviour in a mixture, an activity coefficient can be used [15]. Rault's law, for instance, is based on the assumptions that the vapour phase is an ideal gas and the liquid phase is an ideal solution. By definition, in an ideal mixture, the interactions between each pair of components are the same; consequently, the properties of the mixture can be easily defined as the average value of all involved components. However, there is always slight deviation from the ideal case. Therefore, the Rault's law was modified by introducing an activity coefficient model. Rault's law [15] for phase equilibria is described in Equation {2.8}.

$$y_i P = (x P^{sat})_i \text{.......................................} \{2.8\}$$

Equation 1.7 describes the modified Rault's law. In this case, γ is the activity coefficient parameter which is defined by an activity coefficient model.

$$y_i P = (x \gamma P^{sat})_i \quad \text{.....................................} \{2.9\}$$

Unlike equations of state, activity coefficient models are only used for calculation of fugacities, and they are not able to give all thermodynamic properties such as molar volume, enthalpy, and entropy. Activity coefficient models are also known as Gibbs free energy models. These techniques rely on the second law of thermodynamics, which illustrates that any system is at stable equilibrium only when its Gibbs free energy is minimal. Therefore, using these models demands a minimization of the Gibbs free energy function of the system based on the dependent material balance equations. The RAND algorithm developed by White *et al.* [68] is one the first methods attributed to the Gibbs free energy minimization methods which has been widely modified and used. Gautam and Seider [69] reviewed four Gibbs free energy minimization methods and highlighted the importance of initial guesses in compositions. Barker's isothermal data reduction method [70] is a one-step analytical method which makes direct use of the experimental data [71]. However, Hu *et al.* [20] used this method for isobaric data as well. Many activity coefficient models have been proposed for phase equilibrium calculations. Margules [72], Wilson [73], NRTL [74], and UNIQUAC [75] are the most famous models which have been developed and largely modified. If activity coefficient models are used for VLE data reduction, the vapour phase is usually considered an ideal gas, as stated in Equation {2.9} and the liquid phase is analyzed using these models. In contrast, both phases are modeled if an EOS is used for the modeling approach.

To this end, two main approaches for correlating and reducing experimental VLE data have been introduced. Obviously, each method has its own merits and shortcomings. Equations of state are numerically simple whereas, the activity coefficient models require more calculation because of the optimization process implied in the models. However, activity coefficient models always result in successful convergence for almost any phase equilibrium problem [76].

2.4.5 Combination of Activity Models and Equations of State

The other approach for correlating experimental VLE data is to combine two mentioned methods. This method is also called gamma-phi (γ-φ) approach. Actually, activity coefficient models can only absorb the non-ideality of the liquid phase, so an equation of state is used for the non-ideality of the vapour phase. Equation {2.10} describes the formulation of this method [15]:

$$P\,(y\,\varphi)_i = (x\,\gamma\,P^{sat})_i \quad ....\{2.10\}$$

For determining γ and φ, an activity coefficient model and an equation of state are used, respectively. Due to use of an equation of state, the drawback of this approach is not covering the critical region. However, the merit of this method is the ability to model both the liquid and vapour phases as well as they have the capability to be applied to electrolytes and polymers as well.

2.4.6 Thermodynamic Consistency Test

Many compilations are published each year including isotherm and/or isobar VLE data of mixtures with measured composition in one or both phases. The consistency of a series of VLE data of a multi-component system relies on the Gibbs-Duhem (GD) equation and consequently, the obtained experimental VLE data is called consistent if it satisfies the GD equation. The GD equation is written for a binary mixture in Equation {2.11}.

$$x_1 (d(\ln \gamma_1) / d(x_1)) + x_2 (d(\ln \gamma_2) / d(x_1)) = 0 \quad (\text{const } T, P) \ldots\ldots\{2.11\}$$

Unless the experimental values themselves satisfy the GD equation, the derived values for γ cannot be consistent with the experimental values of γ.

Some methods have been examined in order to test the consistency of collected experimental values for phase equilibrium problems. The consistency tests can be applied to both isobar and isotherm data. Eubank *et al.* [77] and Van Ness [78] comprehensively described methods of testing thermodynamic consistency with respect to GD equations. However, many other researchers also proposed modified methods in their publications [79-82].

For applying a consistency test to a series of experimental VLE data, all thermodynamic properties i.e. the temperature, pressure, and all phase compositions are needed to be measured [77]. However, if even one of the mentioned parameters is not measured, according to van Ness [78] the results were made consistent but without any independent test of the data itself. Therefore, the obtained results from static methods, dew-and-bubble point methods, and any other method, which does not measure all the temperature, pressure, and phase compositions, cannot be tested by a thermodynamic consistency test.

3. Concept of DSC

3.1 Differential Scanning Calorimetry

Thermal analysis (TA) is a very well-known section of material science in which different chemical or physical properties of materials are studied in a heating and/or cooling procedure. Therefore, the properties are measured or estimated within a temperature changing algorithm. Different properties of materials can be analyzed using different methods. Hence, different TA apparatus have been distinguished: thermogravimetry (TG), differential scanning calorimetry (DSC), differential thermal analysis (DTA), dynamic mechanical analysis (DMA), etc. The concept of using DSC was developed by E.S. Watson and M.J. O'Neill [8] in 1962. Differential scanning calorimetry attempts to screen the desired properties of the studied material by measuring the heat flow needed for such processes. In DSC, both the sample pan and the reference pan, which is deliberately chosen empty, undergo a heating/cooling procedure with a same heating/cooling program and the idea is to compare the discrepancies between the measured heat flows of sample and reference and then report it as a thermogram signal. In case of any physical/chemical change in the sample (e.g. absorption, boiling, melting, glass transition, crystallization, and any chemical reactions), the differential heat flow appears as a peak in which its area is proportional to the physical/chemical change and its direction determines whether the event is endothermic or exothermic (i.e. downward and upward correspondingly) [83]. As the technique has been improved, it has been applied in different aspects of science and engineering such as food science [83], lipids and biological membranes [84], molecular recognition and drug design [85], and many chemical engineering fields. A review on different types of early DSC's by Fyans *et al.* [86]

described that the first generation of DSC's included heat flux type and power compensation type. In heat flux DSC's, a well-defined heat conduction path with given thermal resistance is used to measure the heat exchange with the environment. Heat flux DSC's are divided into disk, turret, and cylinder types. In power compensation DSC's, the compensated heat which is supplied from electrical energy, increasing or decreasing adjustable Joule's heat, is being measured [87]. Using DSC is a fast growing analytical technique [86] and recently modulated temperature DSC and high pressure DSC have been developed and used in a fairly large scale. In 1992, Sauerbrunn *et al.* [88] developed the idea of sinusoidal oscillation temperature programmed technique for DSC and it was marketed by TA Instrument under the name of modulated temperature DSC (MTDSC) [89]. Gill [90] reviewed the concept and instrumentation of calorimetry and appropriate information can be found in his publication. In 1992, high pressure DSC also has been examined by Perrenot *et al.* [91] and commercialized by Mettler Toledo Inc. as a new generation of DSC's.

3.2 DSC for Liquids

DSC is widely used for solid samples; however, using DSC for liquid samples has been considered since 1962, as Krawetz and Tovrog [92] proposed the idea to use differential thermal analysis (DTA) for determining vapour pressure data of pure compounds. In 1965, Barrall *et al.* [93] followed the concept of using DTA for liquid samples. Kemme and Kreps [94] also used DTA instrument to determine vapour pressure data of some organic compounds. Seyler [95] indicated that "boiling method" is the principle of using DSC for liquids. Thus, determination of vapour pressure for pure components became the main application of DSC for liquids.

Various approaches have been tried, studied, and suggested while the DSC was being used for determining vapour pressure data of pure liquid compounds. In 1972, Wiedemann [96] used thermogravimetry for determining vapour pressure, combined with the Knudsen [97] effusion method and this combination has widely been used. Morie *et al.* [98] followed the principle of using lids with a pinhole proposed by Perkin-Elmer Corp. [99], so that the sample container remains unrestricted; however, no indication regarding the specifications of the pinhole was made in their publication. They also utilized Carborundum (SiC) as an inert material in order to increase the surface area and prevent superheating. Moreover, making use of open capillary, especially with embedded thermocouples, has been demonstrated to give satisfactory results [95]. Most recently, American Society for Testing and Materials (ASTM) published a standard method, known as ASTM E1782-08 [100], for determining vapour pressure data of pure compounds in which the optimized range for each parameter that affects this method is given. However, it described that each factor itself is a function of instrumentation as well as the purpose of the study. For instance, a higher heating rate may be considered for mixtures as the composition should not change.

3.3 Parameters Affecting the Pure Liquid Samples Results

After the idea of using TA for determining vapour pressure data of liquids had been suggested in general, and DSC in particular, many studies have been done in order to check the amenability of the technique. Based on the fact that DSC is a thermal analysis instrument, heat transfer is the basis of its applications and each parameter which affects the amount of transferred heat will exert significant influence on the results. Obviously, each result is a function of several distinct parameters which can be divided into three main categories; sampling, experimental procedure, and analysis method.

3.3.1 Sampling

Sampling includes many factors which are all about sample size, sample pan configuration, and using inert diluents materials.

3.3.1.1 Sample Size

Seyler [95] investigated the effect of different parameters on the obtained results using DSC. He stated that there is no firm prescription of appropriate sample size, but it depends on the latent heat of the sample as well as test system configuration; however, a 1-15 μL sample is typical. It is added by him that using small amount of sample results in remaining insufficient sample in the pan at the boiling point. Also, large samples are the susceptible to super heating and partial self cooling. ASTM E1782-08 [100] suggests using 1-5 μL/run for liquid samples.

3.3.1.2 Sample Pan Configuration

Sample pan configuration also affects the peak shape of the boiling endotherm of the liquid. It includes the design of sample pan as well as the specifications of the lid. Both the pan and the lid must be inert to the sample.

3.3.1.2.1 Design of Pan

Seyler [95] clarified the effect of pan design by choosing and examining different types of sample vessels. For achieving isotherm boiling, the small surface area-to-volume ratio of pans and maximal vapour head are needed. As such, pans cannot be open or hermetically sealed. Also, sealing the pan hermetically will result in self pressurizing of the cell before the isotherm is reached and boiling elevation will be encountered [95]. Making the use of open pans could lead to the entire sample evaporating before the isotherm is reached and causing a deviation in the boiling thermogram. Other studies [101-103] also demonstrated that using open or sealed pans were not applicable and did not result in comparable results with the ones attained using other methods. Generally, ASTM E1782-08 [100] insisted on inert sample vessels in which the sample loss is minimal and the development of vapour-liquid equilibrium (VLE) has been promoted.

3.3.1.2.2 Specifications of the Lid

Open pans cause loss of the sample and sealed pans elevate the boiling point as a result of self pressurizing. Thus, the sample pan should be sealed hermetically and simultaneously should let vapour escape to maintain the pressure. As discussed, for improving the use of DSC for liquids, methods like using a capillary and pinholes have been investigated [95, 98, 99]. From the commercial and industrial point of view, using a pinhole is more popular than a capillary. Also, the use of a capillary is more common in DTA, especially when it is modified by inserting thermocouples [91, 92, 94]. The principle of using a pinhole is useful when the diameter of the hole is larger than the mean free path of the generated vapours. Therefore, the vapours can leave the pan. Furthermore, small steel balls placed on the lid's holes have been tested. Designing a pan equipped with steel balls moderates the rate of vapour loss and equates it with the rate of vapour replenishment. Tilinski and Puderbach [102] examined this principle in order to overcome the problems associated with the size of holes. They cited that small holes never generate reproducible results, whereas larger holes result in pre evaporation. Therefore, 1.6 mm diameter steel balls were used which resulted in much more promising results. For ordinary heating rates e.g. 5-10 °C/min the hole size of almost 50 μm is applicable [91, 104]. It is suggested by ASTM E1782-08 that the diameter of the holes should be ≤ 125 μm and for pressures between 5 kPa and 2 MPa the size of 50-75 is more amenable. However, Butrow and Seyler [105] quoted that at pressures below 5 kPa the suggested size of ASTM E1782-08 causes a sliding edge curvature in the peak shape and a larger diameter is preferable. Consequently, the size of holes is a function of the mean free path of the vapours, the operating factors such as pressure, carrier gas and etc, instrumentation, as well as the objectives.

3.3.1.3 Inert Diluents

Morie *et al.* [98] used SiC as an inert diluent in order to improve accuracy. Seyler [95] also declared that using glass beads or powdered ceramic (e.g. alumina or SiC) increases the liquid surface area and plays the role of nucleation sites for boiling which causes less super heating. Also, Barrall *et al.* [106] illustrated that with an inert diluent the vapourization was reduced before boiling so that it retained the liquid sample through surface tension. Inert diluents can match the heat transfer parameters between sample and reference portions of the cell, even after boiling [95].

3.3.2 Experimental Variables

Theoretically, the experimental procedure for any experiment depends on the instrument, materials, safety, as well as the objectives of the experiments. In case of using DSC for liquids, the experimental procedure completely depends on the instrumentation and the goal of the study. To finalize the method, heating rate, carrier gas, and operation time will be discussed.

3.3.2.1 Heating Rate

Heating rate is the key to achieve isothermal boiling. Historically, many studies have been done to find out the appropriate range of heating rate. [94, 95, 98, 101, 102] The suggested range is from 1-10 °C/min; however, the main focus is on the range of 5-10 °C/min. In contrast, Silva *et al.* [107] conveyed that using heating rates below 25 °C/min cause large relative deviation in determination of the vapour pressure of ethyl esters.

Generally, the heating rate itself is a function of sample size and sample pan configuration. Generally, the larger the sample, the greater the heating rate would be. In the case of using a pinhole, the heating rate must be sufficiently small to prevent the diffusion of generated vapour into the carrier gas. Also, the diffusion rate should be less than rate of vapour storage in vacant space in the pan. Moreover, it has to be large enough to lessen the increase in pressure due to production of vapour [103]. ASTM E1782-08 suggests 5°C/min.

3.3.2.2 Carrier Gas

Carrier gas rate influences the mass transfer of vapour generated during the experiment. It seems that it has less of an effect on the results in comparison to the other factors; however, it is not negligible. The flow cannot be too high because evacuation occurs or too low which results in pressurizing the cell. The suggested flow rate is 50-100 mL/min in the literature [102]. The carrier gas must be inert to the sample, unless some specific reaction is desired in the presence of the carrier gas. For instance, oxygen or air is sometimes used for oxidation. Nitrogen, carbon dioxide, and argon are suitable inert carrier gases.

3.3.2.3 Operation Time

Although it seems that operating time is dependent on the heating rate, it should be noted that in some cases, especially when the desired pressure is not ambient pressure, some settling time may be needed. Casserino *et al.* [108] held the sample isothermally for 3 min to let it adjust with the applied pressure. Furthermore, it has been recommended that the sample should undergo a heating procedure which initiates 30 or 40 °C below the estimated boiling temperature [100, 108].

3.3.2.4 Thermal Resistance

In case of reduced pressures, the resistance between the embedded thermocouples in the DSC stage and the sample pan affects the generated results considerably due to higher sensitivity at lower pressures. Using a very thin layer of conductive grease has been tried at pressures below 5 kPa by Butrow and Seyler [105] in order to fulfill this concept.

3.3.3 Analysis Method

Considering all cited precautions and running the experiment result in generation of a peak in the heat flow curve versus time/temperature, which is associated with the boiling point of the liquid sample. The main aim of the analysis is to determine the boiling point(s) of the sample, even though in some cases the enthalpy of phase change should be calculated and analyzed. Tilinski and Puderbach [102] compared the heat of vapourization for different pan configuration. Figure 3.1 shows a heat flow curve for boiling of a pure liquid.

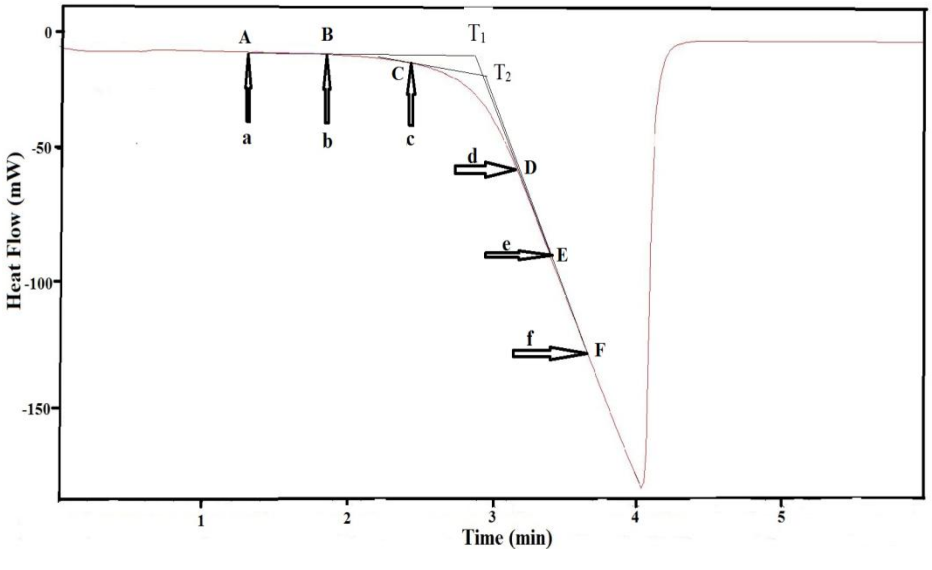

Figure 3-1: Uncertainty in determining the onset value on a heat flow curve

As shown in Figure 3.1, the generated curve consists of three main parts: baseline, peak and the recovery part [95] after boiling. Baseline, theoretically, is a straight line which commences from the beginning of the experiment and lasts until the main peak. However, by the reason of pre evaporation or pre boiling of the liquid sample, it is not a straight line, but it becomes a curve. The baseline deviates from the straight line, especially as it gets closer to the peak. That is, points *A*, *B* and *C* are not located on a straight line in Figure 3.1. The second part of the curve is the peak where boiling takes place. The peak starts from the end of baseline (i.e. point *C*) and looks like a downward asymmetric parabola. The end part is where the entire sample has been evaporated and all vapours have been from the pan/hole. As of this point, it is a straight line but at a higher level than baseline so that there is no sample in the pan.

To this end, the generated curve described above should be evaluated to find desired data. Since the very first publication [98], the boiling temperature is determined by analyzing the extrapolated onset temperature on the heat flow curve. The onset value is the temperature of a point at which two tangents, one from the baseline and the other one from the sliding part of the peak intersect each other (i.e. T_1 or T_2). The onset value is believed to be the boiling point since the boiling approximately starts at this point.

Although deciding on the sample size and heating rate are very important, analyzing the results are more challenging in case of sensitivity and precision. As shown in figure 1, by choosing different combinations of any two points; one from *a*, *b*, and *c* and the other from *d*, *e*, and *f* give different values e.g. T_1 and T_2 in this figure. Therefore, considering the onset value as boiling temperature can be questioned and uncertainty also restricts the use of this technique. The problem originates from the deviation in the baseline which is itself a result of pre evaporation of the liquid. This problem has been neglected in most of the publications by stating the expression that the extrapolated onset value has been chosen as boiling temperature. However, this drawback has been discussed by Falleiro *et al.* [109] through using the technique for determination of VLE data of fatty acids. They chose different points on the baseline and concluded that the difference of 1 °C can be shown in the extrapolated onset value by choosing various tangent lines. They added that this discrepancy can be handled by controlling heating rate and using the pinhole lids.

3.4 Using DSC for Liquid Mixtures

In the previous sections, the parameters which are involved in determining the onset value of a given DSC thermogram have been discussed. Although there is potentially a pre boiling problem in this technique, using DSC for determining vapour pressure data of pure liquids has been widely used, especially for pure organic compounds [102, 104, 108]. Boiling method is the concept of using DSC for liquids [12] and therefore it can be extended to mixtures as well. Mixtures also boil at their boiling points. The boiling point of a binary mixture is usually somewhere between the two boiling points of the pure compounds, unless the system contains an azeotrope. Therefore, it seems that using DSC can determine the boiling point of the mixtures as accurate as the boiling point of the pure compounds. However, in case of mixtures, the most volatile compound is expected to boil because as stated, usually the boiling point of the mixture is above the boiling point of the most volatile compound. Also, pre boiling can change the compositions of the involved chemicals. In other words, a dynamic equilibrium is promoted while using DSC [109], so the equilibrium compositions of the compounds are not the exact initial compositions.

To this end, there is a hesitation towards using this technique for mixtures [27]. Nevertheless, this method has recently given successful outcomes for determining VLE of fatty acids and ethyl esters [107, 109] which ruled out the hypothesis that using DSC should be restricted to pure compounds.

3.5 Using DSC Is a Total Pressure Measurement Analysis

A system is at a dynamic equilibrium when it is always at equilibrium (in this case the vapour and liquid phases are at equilibrium), but not at a unique equilibrium. Considering the sample pan as a system, the vapour and the liquid of each component are at equilibrium at all compositions as the liquid boils. However, the sample pan is considered an open system from which the vapour is going out; therefore, in contrast to conventional equilibrium stills, the system never remains at an exclusive state, even though equilibrium always exists between two phases. Consequently, using DSC is a total pressure measurement type for determining VLE and no measurement is done for vapour phase.

As stated in the previous chapter, total pressure measurement type of VLE needs highly accurate measurements of pressure, temperature, and vapour or liquid phase composition. In case of using DSC, temperature is being measured, pressure is controlled, and the liquid composition is determined. Thus, the vapour phase data is being calculated, fitted and inferred from the measured T, P, and x.

Thermodynamic modelling is done based on the measured and known values. Correlation gives the information on vapour phase and the T-xy curve is plotted. Eubank and Lamonte [77] stated when both x and y have not been measured the results are made consistent; however, the data itself cannot be examined independently. Also, Van Ness [78] also clearly described that no consistency test is possible when data for both phases have not been measured. Therefore, no thermodynamic consistency test is able to be applied to this type of VLE data.

4. DSC Validation

As stated in Chapter 3, differential scanning calorimetry has been used for determining the vapour liquid equilibrium of binary mixtures [109, 107]. It was mentioned in the previous chapter that using this technique has many difficulties and drawbacks which result in uncertainty. In Chapter 3, the uncertainty for determining the onset value in a heat flow diagram was discussed. Ideally, the leading edge of the peak of a heat flow thermogram should be a vertical line in the case of pure components because the temperature remains constant during the boiling event. However, in the case of binary mixtures the leading edge of the peak is not supposed to be a vertical line since the composition is continuously changing during the boiling event. Therefore, it is not reliable to analyze the heat flow thermogram to determine the boiling point(s) of binary mixtures. In this chapter, a new methodology for determining boiling point(s) of both pure components and mixtures is proposed and studied. It is claimed that analyzing sample temperature in lieu of the heat flow curve may overcome the potential drawbacks of using DSC for liquid samples.

Due to the thermal resistance between the sample and the thermocouples, there is always a discrepancy between the actual heat flow and the measured heat flow. As a result, a deviation from the vertical state always occurs in the leading edge of the peak for every thermogram. As a general rule of thumb, Butrow and Seyler [105] suggested -3mW/°C should be the minimum value as an acceptable slope for the leading edge of the heat flow peak. A sharp peak is a result of equality between the rate of sample depletion and the rate of replenishing of vapour until the pan is entirely depleted. This criterion is necessary for accurate measurement of boiling temperatures. However, the onset temperature is extrapolated from the heat flow curve.

In order to overcome the potential problem in determining the onset value, studying sample temperature can be examined. DTA provides a thermogram wherein the temperature difference between the sample and the reference is plotted versus time and/or temperature. In the case of liquid samples, DTA can be effective for determining a precise boiling point since peak broadening (i.e. deviation from a vertical leading edge) can be eliminated [105]. The same concept can be applied to analyze DSC results by evaluating the difference between sample and reference temperatures.

In order to overcome the uncertainties in determining exact boiling points of mixtures, a more rigorous method for analyzing the results has been proposed. The proposed method is based on the fact that the only reliable and unchanged experimental parameter is the heating rate. The idea is illustrated in Figure 4-1 for a binary mixture.

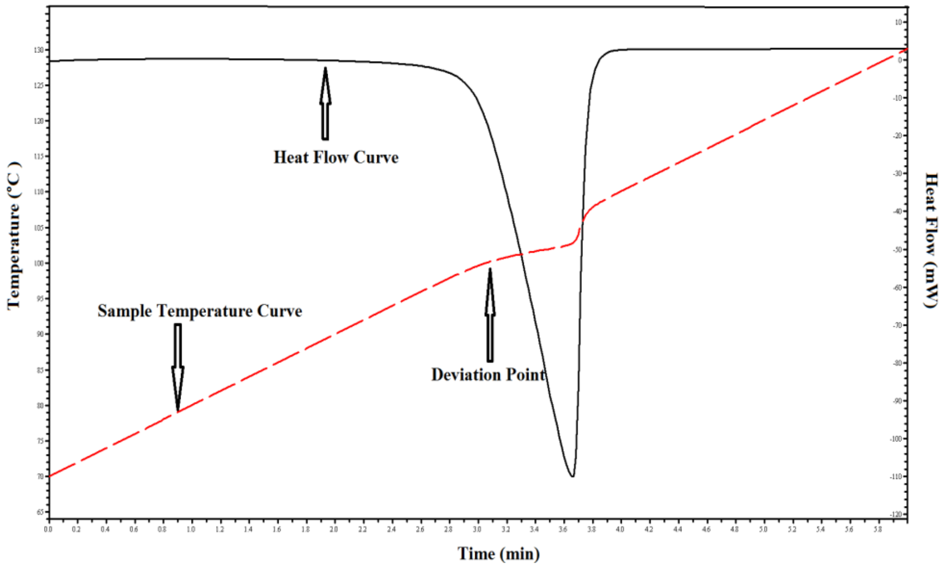

Figure 4-1: Elaborating on the sample temperature analysis and determining the deviation point of a binary mixture

If the heating rate is constant during the experiment, both the sample and reference pans are being heated according to the same temperature program. Thus, the reference temperature curve is a straight line with a constant slope: the heating rate. As shown in Figure 4-1, the sample temperature curve is a straight line as long as there is no phase change and/or the sample is completely evaporated. The liquid sample is being heated like a solid body when no phase change takes place; even though the sample undergoes pre evaporation. However, when the vapour pressure of the liquid equals the ambient pressure, the liquid starts to boil at a constant temperature. Hence, when the sample temperature of a pure compound is monitored by DSC, it becomes a horizontal line until the boiling ends. However, Figure 4-1 shows the sample temperature curve for a binary mixture. As stated, the composition always changes during the boiling because of the dynamic equilibrium and as such, the boiling region of the sample temperature generally becomes a curve as shown in Figure 4-1. When the last droplet of the liquid changes to vapour, the empty sample pan is again being heated like a solid body. Therefore, its slope returns to the original value (i.e. the heating rate). Figure 4-1 demonstrates that analyzing sample temperature in lieu of the heat flow curve results in a more precise determination of the exact transition point. Consequently, the exact deviation point on the sample temperature versus time diagram can be determined and the observed uncertainty resulting from studying heat flow is reduced and/or eliminated.

As shown in Figure 4-1, a very small region in the vicinity of the exact boiling temperature should be considered, which is referred to herein as the scrutinized range. However, the difference between sample and reference temperatures should be considered at all points to find the exact point at which the sample temperature deviates from the reference temperature. Therefore, first and second derivatives of the difference between sample and reference temperatures were calculated to detect the inflection point analytically. Figure 4-2 illustrates the methodology for determining the exact deviation point.

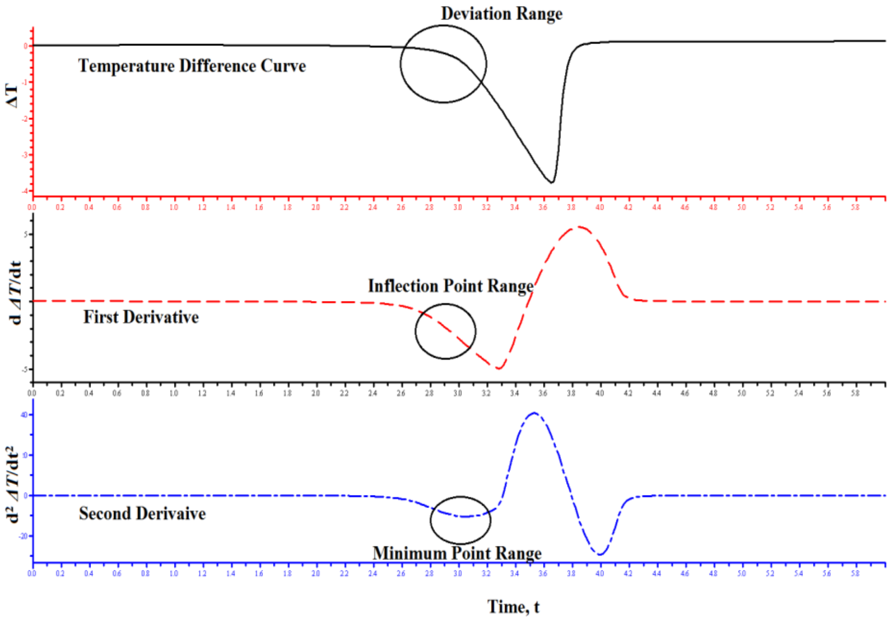

Figure 4-2: Determining the exact deviation point of the sample and reference temperatures difference curve

By definition, the boiling point is the point at which the sign of the slope of the temperature difference changes. From a mathematical point of view, this corresponds to an inflection point on the first derivative function and/or curve. The inflection point of a curve is the maxima or minima for its derivative. Therefore, the transition point is given by the minimum point of the second derivative curve as shown in Figure 4-2. In order to find the temperature value at the minimum point, first and second derivatives of the temperature difference were extracted from the instruments STARe software. Then, the raw data for these three curves were imported to an Excel file. The first minimum point was then found using the plotted curve, and corresponding sample temperature was considered as the boiling point. In mixtures, sometimes more than one peak appears. The first peak corresponds to the initial boiling point of the mixture (e.g. bubble point) and the others are associated with the less volatile components because the more volatile component is preferentially evaporated from the liquid phase during the earlier stages of the process.

Past inaccuracies originated from the inevitable pre evaporation problem. Using specific sample pan configurations (i.e. using pinholes and capillaries) as well as increasing the heating rate and other experimental parameters diminishes the magnitude of this problem. However, the uncertainty of the resulting boiling points is still unacceptable, especially in the case of mixtures. Evaluating the sample temperature omits the effect of pre boiling on the results, but not the problem itself. Moreover, replication can improve the confidence in the results and assures more reproducible, results. Replicating the runs and evaluating all given thermograms for a specific mixture allow the analysis method to be more accurate in the case of finding the exact deviation point.

4.1 Apparatus

4.1.1 High Pressure (HP) DSC

An HP DSC1 manufactured by Mettler Toledo Inc. was used for this work (see Table 4-1 for specifications).

Table 4-1: Specifications for HP DSC used in this work

Item	HP DSC 1 High Pressure Differential Scanning Calorimeter
Company	Mettler-Toledo Inc.
Catalog Number	HP DSC 1
Temperature Range	22 °C to 700 °C
Pressure Range	0-10 MPa
Quantity	EA
Principle	Fast Heating/Cooling DSC 1 Furnace
Measuring Range	+/- 350 mW or +/- 160 mW (at 100 °C)
Heating Rate	0.1 to 50 K/min
Cooling Rate	Inquire

4.1.2 Digital Pressure Transducer

The average ambient pressure in Edmonton is approximately 700 mmHg, so pressurized N_2 gas was used to compensate for the 60 mmHg difference with the standard atmospheric pressure. The ambient pressure was measured using a CPE 1114 Fisher Scientific barometer. A Heise digital pressure gauge (0-10000 kPa) calibrated with Ruska dead weight tester ($\overline{\Delta P} = 0.26\ \%$) was used to measure the system pressure (i.e. the pressure exerted by N_2 gas).

4.2 Calibration of DSC Thermocouples

The calibration of the HP DSC thermocouples was done by measuring both the melting points and the enthalpies of fusion of Indium and Zinc using the standard procedure recommended by the instrument manufacturer at ambient pressure. The calibration procedure was repeated three times for both materials to improve the accuracy of the temperature and heat of fusion measurements. Table 4-2 shows the information regarding the acceptable criteria for each component used in calibration of HP DSC 1. For all components, the given criteria in Table 4-2 were satisfied every time. Moreover, the calibration was done every two weeks.

Table 4-2: Calibration Criteria for HP DSC 1

Material	Onset Temperature (°C)	Heat Flow (J/g)
Indium	156.6 ± 0.3	28.45 ± 0.6
Zinc	419.6 ± 0.7	107.5± 3.2

4.3 Pans and Lids

Hermetic 40 μL aluminum pans were used. In order to overcome pre-boiling effects lids containing a pinhole were used, which allows the sample to have the same pressure as the equipment. The diameter of the pinhole is 50 μm which is made by a laser. Both pans and lids were also manufactured by Mettler Toledo Inc.

4.4 Chemicals

As mentioned, for validating this technique the VLE data for three binary mixtures was collected, studied and benchmarked against published data in the literature [9-14]. The mixtures are methanol-water, isopropanol-water and cyclohexane-toluene. The chemicals used in this study were methanol (CAS No. 67-56-1 and LOT No. 105861), isopropanol (CAS No. 67-63-0 and LOT No. 106259), cyclohexane (CAS No. 110-82-7 and LOT No. 106846) and toluene (CAS No. 108-88-3 and LOT No. 106080). The first two were purchased from Fisher Scientific Canada and the toluene and cyclohexane were purchased from Sigma Aldrich. The water was Reverse Osmosis water (18.2 MΩ).

4.5 Sample Preparation

Different molar compositions between 0 and 1 of each component were prepared for this study. First the component with a higher boiling temperature was added to a vial followed by the one with the lower relative volatility to reduce the effect of evaporation as much as possible. The compositions were determined by recording the weight of each component using a Sartorius CP224S analytical balance. The prepared samples were mixed by shaking just before being introduced into the pan in order to ensure a uniform composition. According to the ASTM E1782-08 method, the amount of sample for each run should not exceed 5 μL. In this study, the maximum amount of sample was introduced to the pan for each run in order to diminish the effects of pre-boiling. A Mettler Toledo XS105 Dual-Range analytical balance was used for weighing the amount of liquid sample in the pan. The lid was hermetically sealed to the pan using a sealing unit manufactured by Mettler Toledo Inc.

4.6 Experimental Procedure

After sample preparation and pan sealing, the pan was located in the DSC chamber and, after sealing the chamber, the pressure was set by connecting the nitrogen cylinder to the DSC. Then, after stabilizing the pressure, the desired method was executed using the STARe version 9.0 software. The method was determined by the difference in the boiling temperatures of the two components in the mixture. As suggested [100, 108], the temperature program was initiated at least 30 °C before the boiling point of the lighter component. Furthermore, the temperature program ended at 30 °C after the boiling point of the heavier component to allow the peak to fully resolve. Even though the ASTM E1782- 08 method recommends 5 °C/min as the heating, a heating rate of 10 °C/min has been chosen for all experiments in this study. In the case of pure water, it was shown that there is no difference in the results using a heating rate in the range of (5-10) °C/min. Therefore, in order to accelerate data collection a heating rate of 10 °C/min was chosen. Also, a faster heating program should help minimize the pre-boiling effects for mixtures since, there would be less vapour due to gradual evaporation. After each experiment the pan was removed when the temperature reached the ambient temperature as stated in the HP DSC1 manual. Cooling was done using a chiller filled with ultra distilled water which operated at a constant temperature of 15 °C.

4.7 Tuning the Technique with Pure Water

First, pure water was used in order to test and tune the method. The boiling temperature of pure water was determined as a function of pressure. Table 4-3 shows the results for pure water at different pressures. It is notable that the effect of dissolved gas can be studied with water since a large amount of gas is always dissolved in pure water. The results in Table 4-3 demonstrate that the method is valid for pure water. The ASTM E1782- 08 method states that this technique must pass the water test. As these results imply, the technique is not influenced by dissolved gases. It is mentioned in Chapter 2 that in dew and bubble point methods of determining VLE data, thorough degassing is critical in order to obtain accurate results. As there is no sampling in dew and bubble point methods, the analysis for these types of experiments relies only on temperature and/or pressure measurements. As a result, temperature and pressure measurement must not be affected by dissolved gas effects. Based on these results for water, DSC measurements are not affected by dissolved gases when measuring boiling point(s).

Table 4-3: Boiling temperature of pure water as a function of pressure measured using the proposed DSC method

Pressure (kPa)	Temperature (°C)		Absolute Error %
	Wagner and PruB[110]	Present Study	
92.9	97.76	97.82	0.0511
94.1	97.92	98.06	0.1430
101.3	100.00	100.01	0.0100
395.0	143.16	143.21	0.0349
585.0	157.84	157.83	0.0063
592.0	158.30	158.51	0.1327
791.0	169.94	169.38	0.3295
1091.0	183.70	183.29	0.2232
1392.0	194.78	194.26	0.2670
1689.0	204.00	203.20	0.3922
2088.0	214.56	213.26	0.6059

The results for pure water have also been examined in terms of reproducibility. Three replications were done for measurement of boiling point at various pressures. The maximum deviation indicates that the results obtained from DSC measurement are valid. Table 4-4 shows the maximum deviation values at different pressures.

Table 4-4: Standard deviation of pure water measurements

P (kPa)	Temperature (°C)	Maximum Deviation (°C)
92.9	97.82	0.01
93.0	97.84	0.05
93.5	97.94	0.05
94.1	98.06	0.02
101.3	100.00	0.01

4.8 Results for Binary Mixtures

As stated, three binary mixtures consisting of methanol-water, isopropanol-water and cyclohexane-toluene have been chosen and studied. The first two systems are aqueous mixtures of an alcohol and the last one is a mixture containing hydrocarbons. The isopropanol-water system contains an azeotrope which has been captured by this technique very accurately. The obtained *T*-*x* data were correlated using different activity coefficient models including Margules, Wilson, van Laar and NRTL. The thermodynamic modeling was done using the bubble point measurements algorithm for constant pressure developed by Smith *et al.* [15]. For this thermodynamic modeling, vapour pressure data for all pure components is needed. The Antonie equation was used for the vapour pressure term in thermodynamic modeling [15]. All of the mentioned activity coefficient models showed the ability to model the experimental data very well. However, the best model in terms of mean deviation of temperature has been chosen for each mixture. The minimization was done using a forward-tangent Newton method with a convergence tolerance of 1.00×10^{-7} °C^2 for the following objective function:

$$\mathrm{OF} = \sum_{\mathrm{i}} (\mathrm{T}_{\mathrm{calc,i}} - \mathrm{T}_{\mathrm{exp,i}})^2$$

Figure 4-3 shows the *T*-*xy* curve for the system containing methanol and water. Table 4-5 also gives the raw experimental *T*-*x* data for this system.

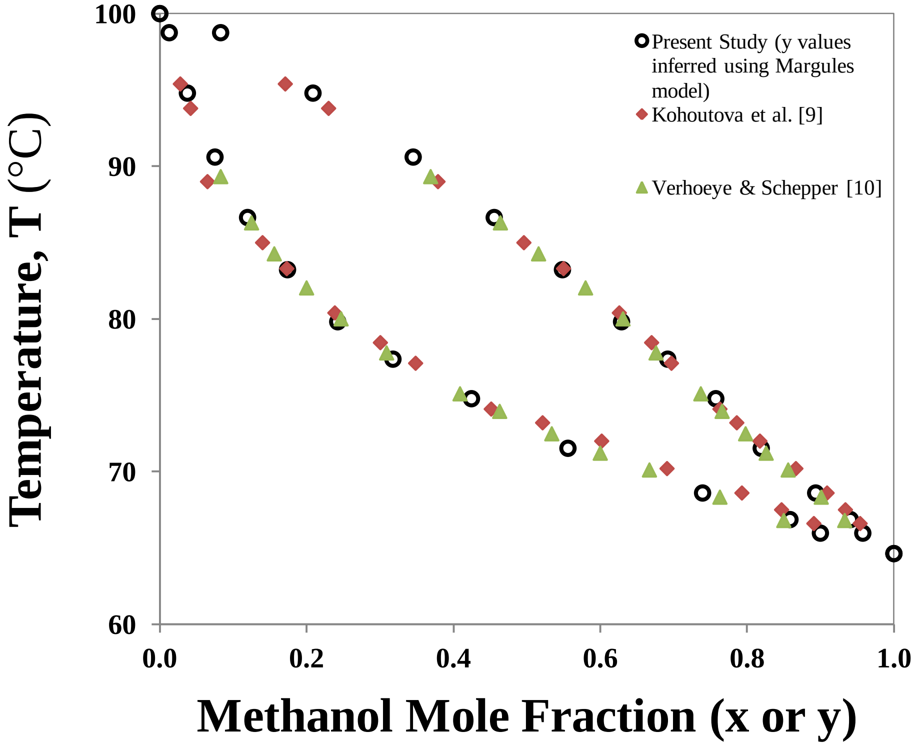

Figure 4-3: *T-xy* curve for the methanol-water system at *P* = 760 mmHg, fitted using the Margules activity coefficient model

Table 4-5: Experimental *T-x* data for the methanol-water system at *P* = 760 mmHg

$x_{Methanol}$	T (°C)	$x_{Methanol}$	T (°C)
0.0000	100.01	0.3176	77.37
0.0129	98.76	0.4246	74.78
0.0376	94.80	0.5560	71.53
0.0752	90.61	0.7394	68.60
0.1196	86.65	0.8584	66.86
0.1740	83.23	0.8999	65.97
0.2424	79.82	1.0000	64.63

Figure 4-4 is the *T-xy* curve for the isopropanol-water system. As mentioned, this system contains an azeotrope at $x_{isopropanol}$ = 0.68.

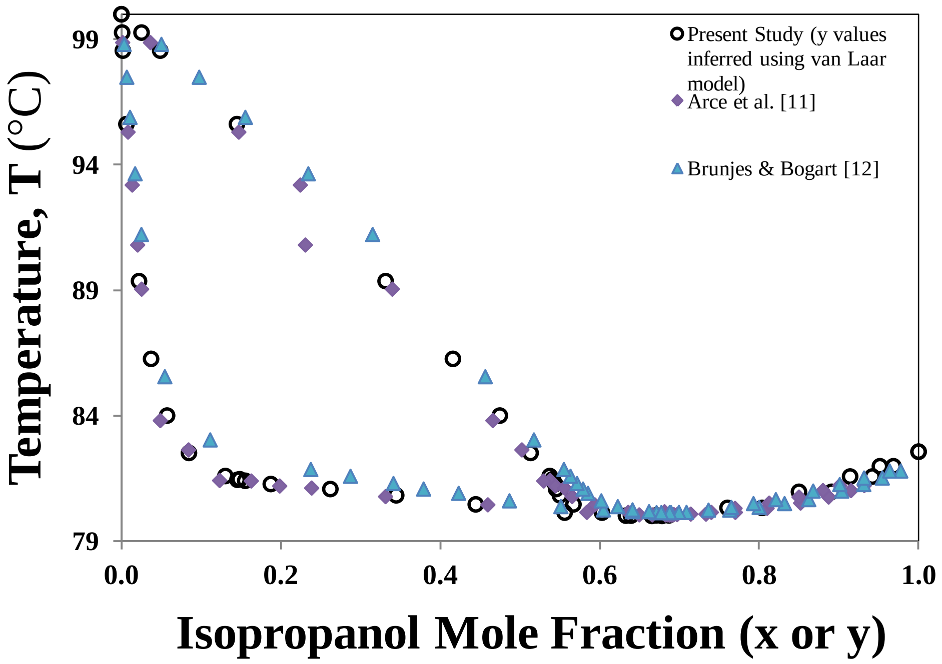

Figure 4-4: *T-xy* curve for the isopropanol-water system at *P* = 760 mmHg fitted using the van Laar activity coefficient model

Table 4-6 shows the experimental raw data for the system consisting of isopropanol and water. The azeotrope point can be identified from these data.

Table 4-6: Experimental *T-x* data for the isopropanol-water system at *P* = 760 mmHg

$x_{isopropanol}$	T (°C)	$x_{isopropanol}$	T (°C)	$x_{isopropanol}$	T (°C)
0.0000	100.00	0.1304	81.59	0.6329	80.01
0.0009	99.27	0.1485	81.44	0.6781	80.00
0.0018	98.55	0.1553	81.40	0.6868	80.02
0.0063	95.62	0.1874	81.27	0.8037	80.32
0.0221	89.36	0.2621	81.07	0.8909	80.96
0.0372	86.26	0.3447	80.82	0.9420	81.57
0.0573	84.00	0.4445	80.46	0.9685	81.98
0.0847	82.51	0.5560	80.13	1.000	82.56

And finally, the *T-xy* curve and the experimental *T-x* data for the system cyclohexane and toluene are shown in Figure 4-5 and Table 4-7, respectively.

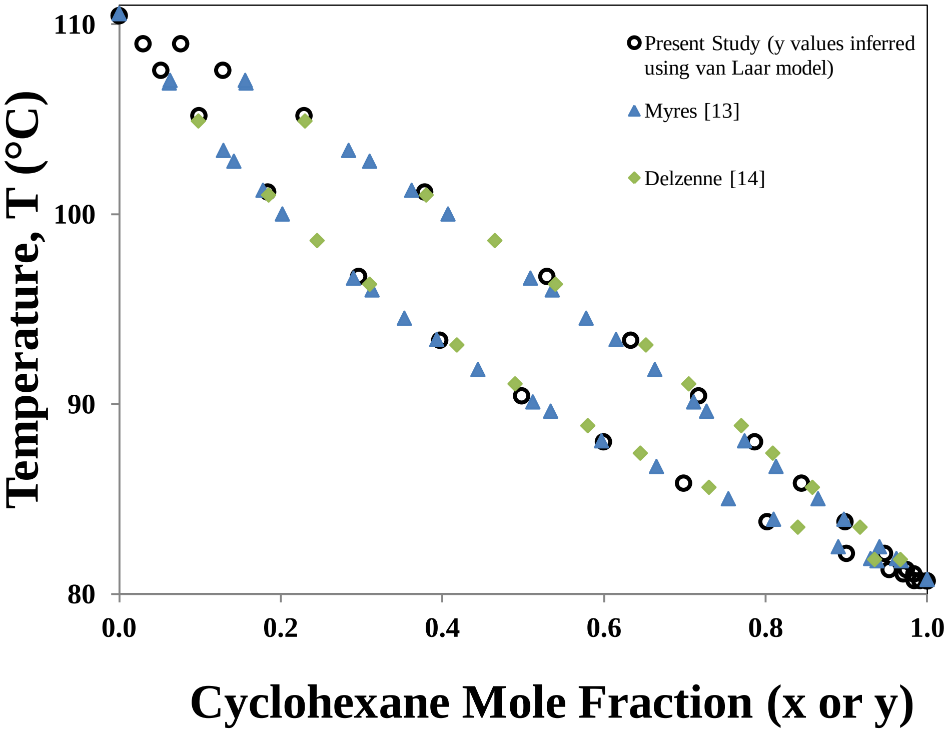

Figure 4-5: *T-xy* curve for the cyclohexane-toluene system at *P* = 760 mmHg fitted using the van Laar activity model

Table 4-7: Experimental *T-x* data for the cyclohexane-toluene system at *P* = 760 mmHg

$x_{cyclohexane}$	T (°C)	$x_{cyclohexane}$	T (°C)
0.0000	110.45	0.5994	88.00
0.0295	108.97	0.6985	85.82
0.0515	107.57	0.8018	83.79
0.0987	105.18	0.9000	82.12
0.1838	101.16	0.9530	81.27
0.2964	96.71	0.9703	81.04
0.3968	93.35	0.9839	80.69
0.4981	90.42	1.0000	80.67

Although for the isopropanol-water and cyclohexane-toluene systems the van Laar and for the methanol-water system the Margules activity coefficient models were used for data correlation, the following tables demonstrate that the other activity coefficient models are also able to model the experimental data well. However, the best model was chosen based on the lowest temperature deviation. Therefore, Wilson and NRTL activity coefficient models can be used for modeling these systems as well. Tables 4-8, 4-9 and 4-10 give the activity coefficient parameters for all of these models for each binary pair.

Table 4-8: Activity coefficient parameters for the methanol-water system

G^E Model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	0.6964	0.5931	N/A	0.19
van Laar	0.6958	0.6016	N/A	0.19
Wilson	-164.22	555.31	N/A	0.20
NRTL	55.450	324.59	0.2976	0.19

Table 4-9: Activity coefficient parameters for the isopropanol-water system

G^E Model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	2.4408	0.7965	N/A	0.65
van Laar	2.6872	1.1397	N/A	0.18
Wilson	605.64	1049.9	N/A	0.35
NRTL	-38.68	1490.7	0.3008	0.20

Table 4-10: Activity coefficient parameters for the cyclohexane-toluene system

G^E Model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	0.1611	0.3253	N/A	0.34
van Laar	0.1763	0.3713	N/A	0.42
Wilson	227.60	477.00	N/A	0.40
NRTL	588.10	332.20	0.3364	0.37

4.9 Conclusions

Although many papers have been published in which DSC was used to determine vapour pressure data of pure compounds, there are several potential shortcomings which result in error in the results. Pre-boiling of the liquid sample is the phenomenon with the most influence on the results. Even though different techniques such as using lids containing a pinhole, adding more sample mass and increasing the heating rate even up to 25 °C/min have been tried, the effect of pre-boiling seemed to be inevitable. Also, the difficulty in determining the exact onset value, which is considered to be the transition point, seems to be inevitable as well. That is, there is always arbitrary selection of tangents for determining the onset point as shown in Figure 3-1 in the previous chapter. Therefore, a new method for analyzing raw data obtained from DSC experiments has been proposed in this study. The concept is to analyze the sample temperature curve in lieu of heat flow curve to avoid the effect of pre-boiling. This idea is based on the only constant and reliable variable in such experiments, the heating rate. As the heating rate is constant in this type of experiment, one can determine the deviation point from the temperature curve which indicates the exact transition point. In order to implement this concept, it is better to evaluate the sample and reference temperature difference curve to determine the deviation point since the reference temperature curve is always a line with constant slope. Taking first and second derivatives of the difference curve identifies the exact transition point(s). Mathematically, the deviation point in the difference curve is the point at which the direction of its first derivative changes. As such, this point would be the inflection point of the first derivative curve, which is exactly the minimum point of the second derivative curve. Therefore, the transition point can be identified by extracting raw data for each run and determining the first minima of the second derivative.

This idea was used to determine the boiling point of pure water as a function of pressure. The results are in agreement with previously reported data which demonstrates the accuracy and validity of the method for pure water. It is notable that vapour pressure measurements using DSC for pure liquids are not affected by the presence of dissolved gases in the liquid. The method proved accurate for a component that has many dissolved gases (water) and therefore it can be used reliably for other liquids. Each data sample for all mixtures is replicated three times for improved accuracy as stated in the previous chapter. Therefore, the proposed methodology passes the tests for pure water both in accuracy and reproducibility. Also, the method has the ability to be used for different types of binary mixtures including aqueous mixtures i.e. methanol-water and isopropanol-water as well as non-aqueous mixtures such as cyclohexane-toluene. Furthermore, it has been proven that the method is valid even for highly non-ideal systems like isopropanol-water which contains an azeotrope.

Therefore, the suggested method is valid and accurate enough for determining VLE data of binary mixtures. In comparison to the conventional VLE data collection methods, this method has many advantages. Small sample amount, rapid data collection and no dissolved gas effect are the main advantages of using DSC for determining VLE data. In most of the conventional methods large amount of samples are needed (at least 100 mL) and also most of them take an hour to reach equilibrium and need sampling for their analysis.

5. VLE Data for Binary Pairs of 1-Hexanol, 1-Heptanol, 1-Nonanol and 1,3-Propanediol

As mentioned in Chapter 1, a two-step biopolymer reaction results in the production of a suite of by-products including various glycols and n-alcohols. In order to develop a suitable separation process, vapour liquid equilibrium data is needed for the various binary pairs, which would then allow for the design of a suitable separation sequence. Furthermore, in the previous two chapters a new method for determining VLE data of binary mixtures has been proposed and studied. The use of differential scanning calorimetry has been proven to be suitable for determining VLE data of binary pairs. As such, the proposed method was used for determining the binary pairs consisting of the by-product of the indicated biopolymer reaction. These by-products are 1,3- propanediol, 1-nonanol, 1-hexanol and 1-heptanol. Combining each two of these compounds results in be six different binary mixtures for which the VLE data should be collected. It is notable that exactly the same instrumentation and criteria stated in Chapter 4 were used for collecting data of these six mixtures. The chemicals used were 1-hexanol (CAS No. 111-27-3 and LOT No. 10159527), 1-heptanol (CAS No. 111-70-6 and LOT No. 10154047), 1-nonanol (CAS No. 143-08-8 and LOT No. 10148873) and 1,3-propanediol (CAS No. 504-63-2 and LOT No. 10145787), all purchased from Alfa-Aesar.

5.1 Data Correlation Using Activity Coefficient Models

First, the collected experimental *T*-*x* data are correlated using various activity coefficient models including two-constant Margules, van Laar, Wilson and NRTL. For plotting *T*-*x* curves, a model is chosen based on the lowest mean temperature deviation. As stated in Chapter 2, the iteration process for correlating the experimental data using the activity coefficient models requires vapour pressure data. The volumetric parameter in the Wilson model is another piece of data which must be known for applying the Wilson activity model. Table 5-1 gives the volumetric parameter for the Wilson model [111].

Table 5-1: Volumetric coefficient for the Wilson model

Compound	V_i
1-hexanol	125.23
1-heptanol	141.35
1-nonanol	174.37
1,3-propanediol	73.5

In the case of 1,3-propanediol the volumetric coefficient is not reported in the literature; however, this number is interpolated using the numbers for 1-propanol, 2-propanol, 1,2-propanediol and glycerol. These components can be categorized based on the number of –OH sub-groups [111]:

1-propanol & 2-propanol < 1,2-propanediol & 1,3-propanediol < glycerol

Therefore V_i has been estimated for 1,3-propanediol based on the above categorization.

Table 5-2 gives the experimental *T-x* data as well as the inferred value for vapour composition, *y*, using the van Laar activity coefficient model the 1-hexanol/1-heptanol system at P = 760 mmHg. Figure 5-1 is the *T-xy* curve for the system containing 1-hexanol and 1-heptanol using the van Laar model and Table 5-3 shows the interaction parameters for various different activity coefficient models. As shown in Figure 5-1, this binary pair is well behaved with no azeotrope present in this system. There is no previously reported data for this system at P = 760 mmHg to compare our results to, although the results are consistent with expectations for a mixture of two similar molecules. 1-heptanol has a longer molecular chain than 1-hexanol, however, the difference in their boiling point is not considerable (i.e. 19.33 °C). Therefore, it is expected that the *xy* curve for this system would be very close to the 45° line.

Table 5-2: Experimental *T*-*x* data and inferred *y* values using the van Laar activity coefficient model for the 1-hexanol/1-heptanol system at P = 760 mmHg

$x_{Hexanol}$	T (°C)	$y_{Hexanol}$	$x_{Hexanol}$	T (°C)	$y_{Hexanol}$
0.0000	176.33	0.0000	0.5999	162.82	0.7312
0.0175	175.46	0.0327	0.6999	160.79	0.8062
0.0302	175.36	0.0560	0.8006	159.60	0.8750
0.0505	174.66	0.0917	0.8992	158.16	0.9397
0.0996	173.26	0.1733	0.9497	157.70	0.9679
0.2004	170.90	0.3209	0.9710	157.16	0.9822
0.2971	168.52	0.4421	0.9850	157.00	0.9908
0.3991	166.52	0.5525	1.0000	157.00	1.0000
0.4991	164.73	0.6470			

Table 5-3: Binary parameters for different activity coefficient models for the 1-hexanol/1-heptanol system at P = 760 mmHg

G^E model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	0.0716	0.0874	N/A*	0.15
van Laar	0.0565	0.1194	N/A	0.14
Wilson	-102.11	186.65	N/A	0.15
NRTL	267.28	-194.24	0.3001	0.15

* *This parameter, α, is not applicable in Margules, van Laar and Wilson activity models.*

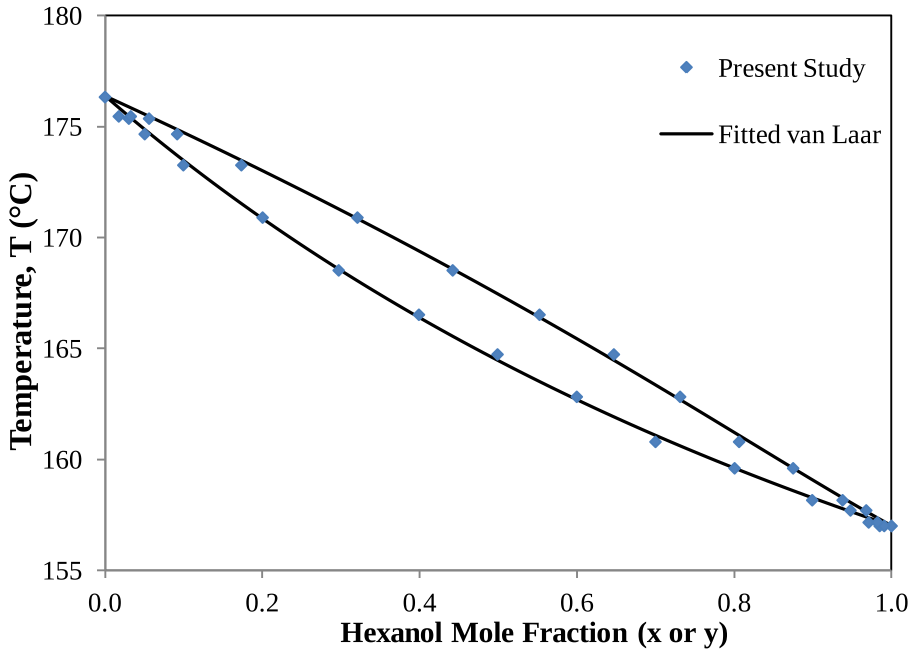

Figure 5-1: *T*-*xy* curve for the 1-hexanol/1-heptanol binary pair at *P* = 760 mmHg, correlated using the van Laar activity coefficient model

Table 5-4 shows the experimental *T*-*x* data and the inferred values for *y* using the Margules activity coefficient model for the 1-hexanol/1-nonanol system at *P* = 760 mmHg. Table 5-5 summerized the binary interaction parameters for different activity coefficient models. Figure 5-2 shows the *T*-*xy* curve for the 1-hexanol/1-nonanol system using the Margules model. The molecular chain of 1-nonanol is longer than 1-hexanol and therefore its boiling point is greater than 1-hexanol. The results show that this system also does not contain an azeotrope.

Table 5-4: Experimental *T*-*x* data and inferred *y* values using the Margules activity coefficient model for the 1-hexanol/1-nonanol system at *P* = 760 mmHg

$x_{Hexanol}$	T (°C)	$y_{Hexanol}$	$x_{Hexanol}$	T (°C)	$y_{Hexanol}$
0.0000	213.38	0.0000	0.5985	171.95	0.9138
0.0206	212.77	0.0449	0.6980	167.03	0.9479
0.0331	211.70	0.0733	0.8000	163.08	0.9713
0.0525	210.91	0.1188	0.8991	159.43	0.9874
0.1015	208.43	0.2374	0.9500	158.07	0.9941
0.2026	200.94	0.4722	0.9702	157.63	0.9966
0.3120	191.77	0.6698	0.9840	157.12	0.9982
0.4007	184.77	0.7800	1.0000	156.93	1.0000
0.5012	178.99	0.8627			

Table 5-5: Binary parameters for different activity coefficient models for the 1-hexanol/1-nonanol system at *P* = 760 mmHg

G^E model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	-0.8142	-0.3682	N/A	0.30
van Laar	-0.8686	-0.4436	N/A	0.36
Wilson	522.09	-677.36	N/A	0.37
NRTL	-636.75	524.28	0.3259	0.40

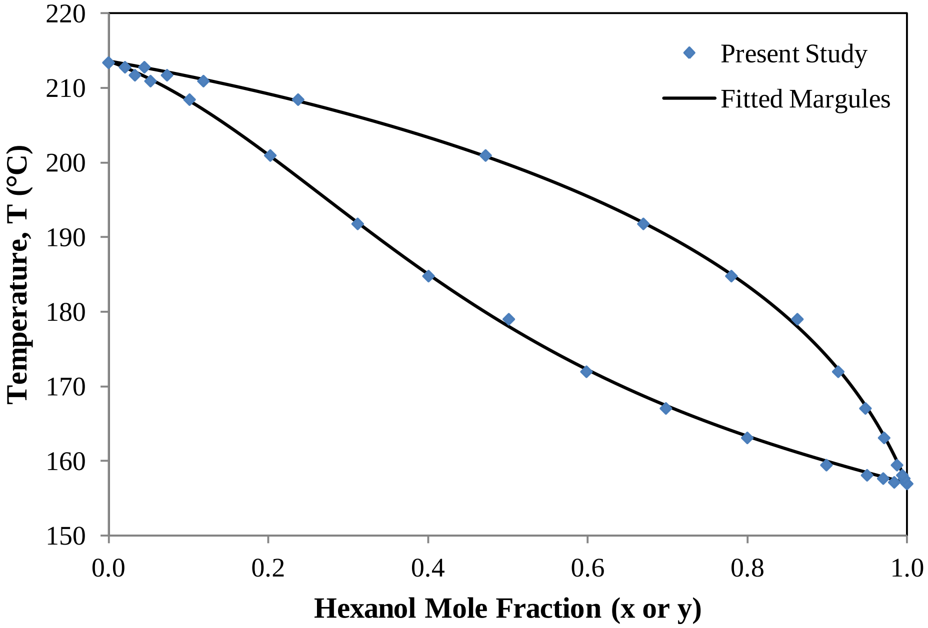

Figure 5-2: *T-xy* curve for the system containing 1-hexanol/1-nonanol at *P* = 760 mmHg, correlated using the Margules activity coefficient model

The experimental *T-x* data and the inferred *y* values are given in Table 5-6 for the 1-heptanol/1-nonanol system. Binary parameters for various activity coefficient models are shown in Table 5-7 for the 1-heptanol/1-nonanol system at *P* = 760 mmHg and the fitted *T-xy* curve for this system is shown in Figure 5-3 using the Margules model. The difference in the number of carbon atoms between 1-heptanol and 1-nonanol causes a relatively large difference in their boiling points. There is no azeotrope for this pair. Figure 5-3 shows that this system is well behaved as well.

Table 5-6: Experimental *T*-*x* data and inferred *y* values using the Margules activity coefficient model for the 1-heptanol/1-nonanol system at *P* = 760 mmHg

$x_{Heptanol}$	T (°C)	$y_{Heptanol}$	$x_{Heptanol}$	T (°C)	$y_{Heptanol}$
0.0000	213.36	0.0000	0.5998	186.95	0.8264
0.0146	212.81	0.0333	0.6959	184.10	0.8785
0.0347	211.80	0.0785	0.8013	180.80	0.9256
0.0487	211.07	0.1095	0.9023	178.11	0.9648
0.0973	208.76	0.2103	0.9485	177.46	0.9816
0.1967	204.02	0.3997	0.9709	176.73	0.9896
0.2963	199.12	0.5498	0.9812	176.48	0.9933
0.4014	194.26	0.6716	1.0000	176.38	1.0000
0.4991	190.01	0.7577			

Table 5-7: Binary parameters for different activity coefficient models for the 1-heptanol/1-nonanol system at *P* = 760 mmHg

G^E model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	-0.1491	0.1062	N/A	0.20
van Laar	0.0079	-2.5058	N/A	0.28
Wilson	211.82	-211.82	N/A	0.36
NRTL	-96.69	93.93	0.3297	0.36

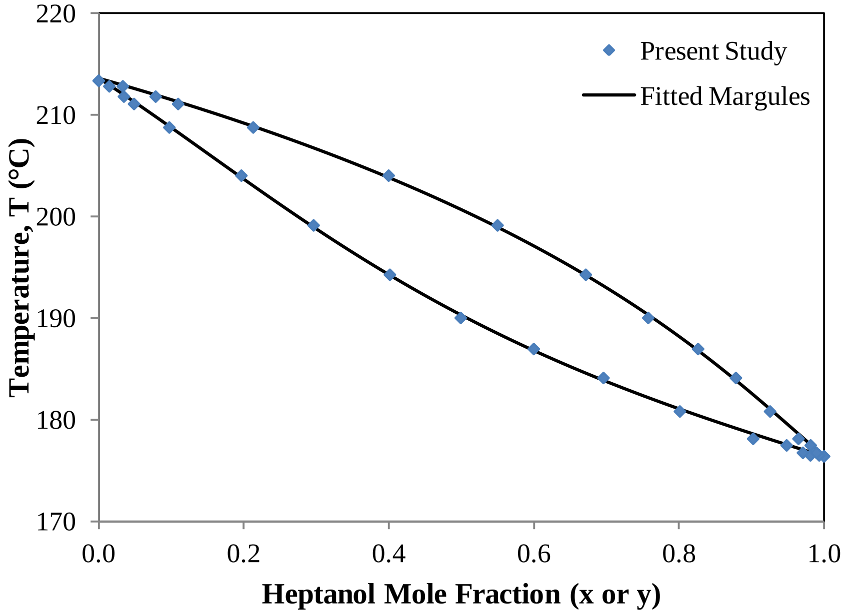

Figure 5-3: *T-xy* curve for the system containing 1-heptanol/1-nonanol at *P* = 760 mmHg, correlated using the Margules activity coefficient model

The data for the ystem containing 1-hexanol/1,3-propanediol is given in Tables 5-8 and 5-9 as well as Figure 5-4. Although 1,3-propanediol has a shorter molecular chain, it has a higher boiling point in comparison to 1-hexanol. This huge difference in their boiling points (i.e. 57.34 °C) results in well behaved *Txy* data without an azeotrope.

Table 5-8: Experimental *T-x* data and inferred *y* values using the NRTL activity model for the 1-hexanol/1,3-propanediol system at *P* = 760 mmHg

$x_{Hexanol}$	T (°C)	$y_{Hexanol}$	$x_{Hexanol}$	T (°C)	$y_{Hexanol}$
0.0000	214.29	0.0000	0.6002	165.49	0.9260
0.0177	212.23	0.0706	0.7000	162.30	0.9496
0.0309	210.94	0.1202	0.7974	159.99	0.9644
0.0516	208.71	0.1942	0.9019	158.59	0.9764
0.0979	203.51	0.3407	0.9470	157.66	0.9832
0.1991	194.33	0.5797	0.9702	157.34	0.9886
0.2998	185.21	0.7325	0.9792	157.11	0.9914
0.4012	177.53	0.8293	1.0000	156.95	1.0000
0.5000	170.34	0.8884			

Table 5-9: Binary parameters for different activity coefficient models for the 1-hexanol/1,3-propanediol system at P = 760 mmHg

G^E model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	-0.3425	0.6076	N/A	0.76
van Laar	0.0976	2.9369	N/A	0.99
Wilson	-832.01	2904.49	N/A	0.61
NRTL	1834.81	-760.09	0.3000	0.26

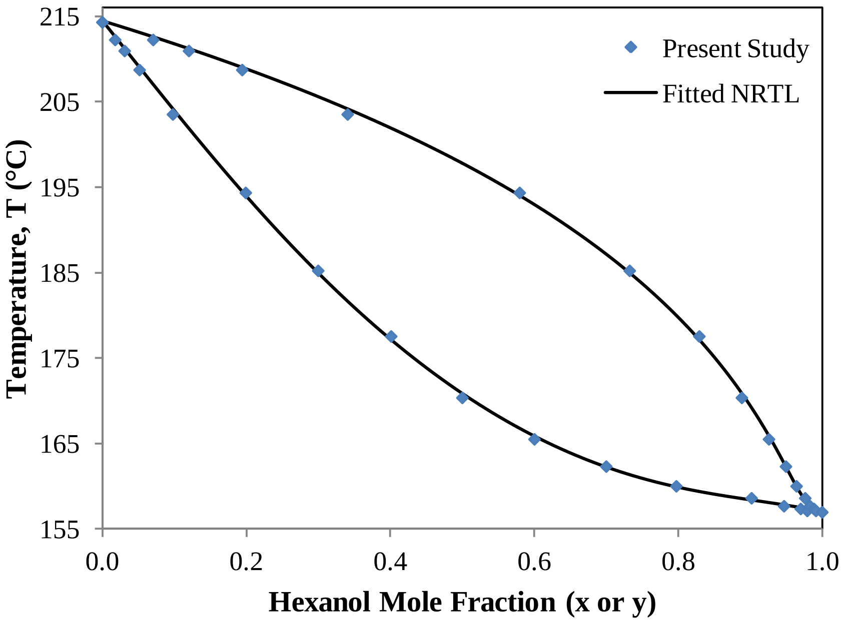

Figure 5-4: *T-xy* curve for the system containing 1-hexanol/1,3-propanediol at P = 760 mmHg, correlated using the NRTL activity coefficient model

The system including 1-heptanol and 1,3-propanediol was fitted using van the Laar activity coefficient model and the resulting *T-xy* curve is shown in Figure 5-5. The experimental data and activity coefficient model binary parameters are summerized in Tables 5-10 and 5-11, respectively. Although these two components belong to different types of alcohols (i.e. 1-heptanol is a linear chain alcohol and 1,3-propanediol is a diol), there is no azeotrope in this system. Moreover, the huge difference in their boiling points results in a well behaved system.

Table 5-10: Experimental *T*-*x* data and inferred y values using the van Laar activity model for the 1-heptanol/1,3-propanediol system at P = 760 mmHg

$x_{Heptanol}$	T (°C)	$y_{Heptanol}$	$x_{Heptanol}$	T (°C)	$y_{Heptanol}$
0.0000	214.26	0.0000	0.6018	185.31	0.8012
0.0187	210.74	0.1117	0.7044	182.11	0.8605
0.0328	208.95	0.1735	0.8063	180.14	0.9135
0.0503	207.07	0.2333	0.8976	178.27	0.9564
0.1027	202.92	0.3534	0.9453	177.31	0.9773
0.1988	198.06	0.4846	0.9670	176.94	0.9865
0.2998	194.32	0.5826	0.9764	176.64	0.9904
0.3989	191.15	0.6631	1.0000	176.40	1.0000
0.4977	188.22	0.7342			

Table 5-11: Binary parameters for different activity coefficient models for the 1-heptanol/1,3-propanediol system at *P* = 760 mmHg

G^E model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	0.7632	0.2079	N/A	0.46
van Laar	0.9857	0.3014	N/A	0.20
Wilson	539.20	79.76	N/A	0.20
NRTL	-397.22	986.42	0.3301	0.30

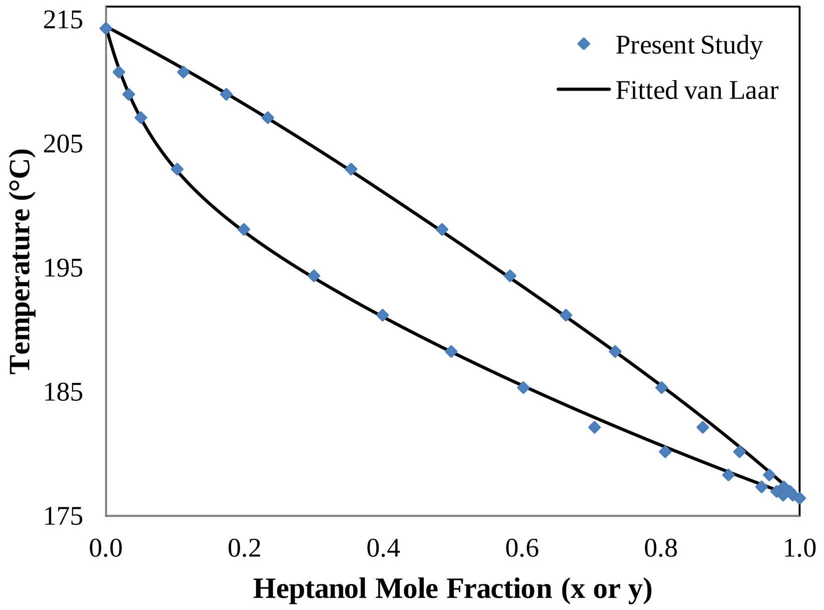

Figure 5-5: *T*-*xy* curve for the system containing 1-heptanol/1,3-propanediol at *P* = 760 mmHg, correlated using the van Laar activity coefficient model

Finally, the data for the 1-nonanol/1,3-propanediol system is shown in Figure 5-6 as well as Tables 5-12 and 5-13. These components have very similar boiling points with a difference of only 0.85 °C. As indicated in Figure 5-6, this binary pair does have an azeotrope at a composition of $x_{\text{nonanol}} = 0.4484$ and a temperature of 201.29 °C.

Table 5-12: Experimental *T*-*x* data and inferred *y* values using the NRTL activity model for the 1-nonanol/1,3-propanediol system at *P* = 760 mmHg

$x_{Heptanol}$	T (°C)	$y_{Heptanol}$	$x_{Heptanol}$	T (°C)	$y_{Heptanol}$
0.0000	214.30	0.0000	0.4184	201.31	0.4423
0.0155	211.94	0.0908	0.4511	201.30	0.4498
0.0309	209.91	0.1571	0.4660	201.36	0.4535
0.0520	207.35	0.2223	0.5952	201.98	0.4962
0.0991	204.61	0.3099	0.7021	202.85	0.5541
0.2024	202.44	0.3885	0.8005	204.59	0.6376
0.2965	201.56	0.4170	0.8925	207.89	0.7588
0.3492	201.40	0.4281	0.9410	209.83	0.8495
0.3718	201.35	0.4326	0.9651	211.27	0.9045
0.3860	201.32	0.4355	0.9873	212.63	0.9628
0.3984	201.31	0.4381	1.0000	213.45	1.0000

Table 5-13: Binary parameters for different activity coefficient models for the 1-nonanol/1,3-propanediol system at *P* = 760 mmHg

G^E model	A_{12}	A_{21}	α	$\overline{\Delta T}$ (°C)
Margules	1.8716	1.0852	N/A	0.13
van Laar	1.9440	1.1811	N/A	0.15
Wilson	450.79	721.46	N/A	0.31
NRTL	-5467.27	7308.79	0.0136	0.13

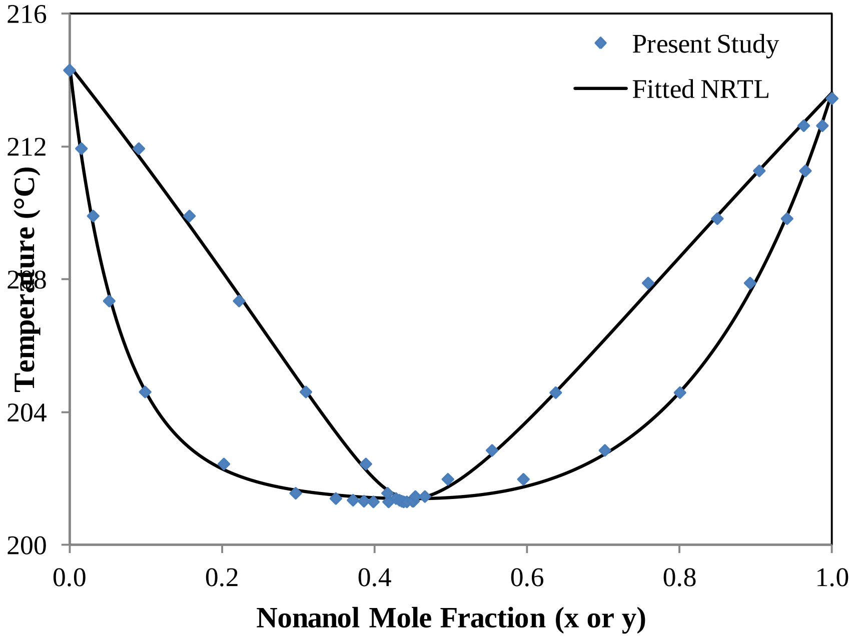

Figure 5-6: *T-xy* curve for the system containing 1-nonanol/1,3-propanediol at *P* = 760 mmHg, correlated using the NRTL activity coefficient model

5.2 Possible Separation Techniques

The azeotrope point is almost at the point at which $x_{nonanol}$ = 0.4484; however, both *T-x* and *T-y* curves are not too close to the 45° line which means that using conventional distillation can separate these two components up to the azeotropic concentration easily. Moreover, it can be concluded that since there is no azeotrope in any of the other binary pairs, distillation is a feasible way to separate all of the other chemicals to a high purity.

5.3 Data Correlation Using Equations of State

As mentioned in Chapter 2, equations of state can be used for equilibrium data correlation of mixtures. It also has been mentioned that the most popular cubic equations of state are proposed by Peng and Robinson (PR) [42] as well as Redlich and Kwong (RK) [40]. The modified

Peng-Robinson EOS proposed by Stryjek and Vera [43] is also explained in Chapter 2, which will be abbreviated as the PRSV equation of state. Using an equation of state for VLE data correlation for a mixture demands a mixing rule which rearranges properties of the pure compounds in order to calculate properties for the mixture. Since the third pure component property in the PRSV EOS, κ_1, is an empirical property of a compound, there is no explicit equation that gives this value in terms of pure compnent properties [112]. Stryjek and Vera gave the value for κ_1 for various compounds in their publication. However, κ_1 values for 1-heptanol, 1-nonanol and 1,3-propanediol were not reported. The value for 1-hexanol is reported to be -0.00237. Therefore, the κ_1 values for each of the compounds have been calculated using experimental vapour pressure data [113-115]. The method of determining κ_1 relies on minimization of mean square deviations of the calculated vapour pressure from the experimental values [112]. However, the empirical nature of κ_1 results in wide dependence to the critical values as well as the experimental values of vapour pressure data. Therefore, the critical properties of the compounds and the calculated values for κ_1 should be used together as they are internally consistent [112]. Table 5-14 gives the values for κ_1. The deviation of calculated vapour pressure and calculated (i.e. $\overline{\Delta P}$) is as below (where *n* is the number of data points):

$$\overline{\Delta P} = \frac{1}{n} \sum (P_{calc} - P_{exp})$$

Table 5-14: Pure component parameters [116]

Compound	T_c (K)	P_c (kPa)	ω	κ_1	$\overline{\Delta P}$ (kPa)
1-hexanol	611.3	3446	0.5586	0.3416	1.083
1-heptanol	632.3	3085	0.5621	0.4128	0.462
1-nonanol	670.9	2527	0.5841	0.7824	0.541
1,3-propanediol	724.0	9500	0.7385	-0.2342	0.637

It is notable that the reported parameters for 1-hexanol in Stryjek and Vera's publication [112] are different than the ones calculated in this study. However, for the sake of consistency the values in Table 5-14 are used for all future calculations in this work. As long as the value for κ_1 is used along with the critical values from which it is calculated, one can use that set of data with confidence since they are internally consistent.

Both the PR and PRSV equations of state were used to correlate the data obtained in this work, and the results are summarized in Table 5-15. The comparison is based on the deviation of calculated values for vapour compositions from the correlated values using the best activity coefficient model described earlier. This table demonstrates that the PRSV EOS is a better model in terms of vapour composition deviation ($\overline{\Delta y}$). With the exception of the 1-nonanol/1,3-propanediol system, the PRSV leads to better results than PR. Table 5-15 also gives the adjustable binary coefficient for both equations of state.

Table 5-15: Binary interaction parameter and vapour composition deviation comparison between PR and PRSV for the systems studied in this work

	$\overline{\Delta y}$		k_{12}	
Mixture	**PR**	**PRSV**	**PR**	**PRSV**
Heptanol/Nonanol	0.013636	0.008969	0.0051	0.0028
Heptanol/Diol	0.002707	0.000958	-0.1372	-0.1452
Hexanol/Heptanol	0.007540	0.004891	0.0157	0.0137
Hexanol/Nonanol	0.019590	0.014280	-0.0429	-0.0459
Hexanol/Diol	0.011598	0.011308	-0.1644	-0.1739
Nonanol/Diol	0.122344	0.122423	-0.1345	-0.1366

5.4 Combination of Equations of State and Activity Coefficient Models

As the data correlation using simple equations of state results in large deviations in some cases, a more advanced mixing rule is required with the equation of state in order to improve data correlation. Stryjek and Vera [112] proposed using Margules (PRSV-M) and van Laar (PRSV-vL) mixing rules along with their equation of state to correlate VLE data for strongly non-ideal mixtures. The combination of PR and these activity coefficient mixing rules has also been studied. Table 5-16 demonstrates that using PRSV with a van Laar mixing rule is the best in almost all of the binary pairs. Using the PRSV with a van Laar mixing rule gives a lower deviation of vapour phase composition. Also, it can be concluded from Table 5-16 that using PRSV-vL is even better than PRSV-M to fit the data for all of the pairs. Since the van Laar mixing rule is more complex than the Margules, it is better to use PRSV-vL for data correlation for all of these binary pairs. Furthermore, using an activity coefficient type mixing rule is better in general because simple vdW mixing rule mentioned in Chapter 2 cannot absorb the non-ideality very well.

Table 5-16: Vapour composition deviation comparison among PR and PRSV and different combinations with different mixing rules

	$\overline{\Delta y}$			
Mixture	**PR-M**	**PR-vL**	**PRSV-M**	**PRSV-vL**
Heptanol/Nonanol	0.013695	0.010437	0.009751	0.007408
Heptanol/Diol	0.001963	0.002700	0.000913	0.000807
Hexanol/Heptanol	0.005675	0.005550	0.003687	0.003662
Hexanol/Nonanol	0.020953	0.013284	0.014893	0.007664
Hexanol/Diol	0.009408	0.006444	0.010315	0.006206
Nonanol/Diol	0.025743	0.008509	0.023446	0.010956

Figure 5-7 shows the combination of PR equation of state and van Laar mixing rule for correlating VLE data of 1-nonanol/1,3-propanediol system. This figure demonstrates that using PR-vL results in a very good agreement with the correlated data using activity coefficient models. Moreover, it can capture the azeotrope point exactly as the inferred data give.

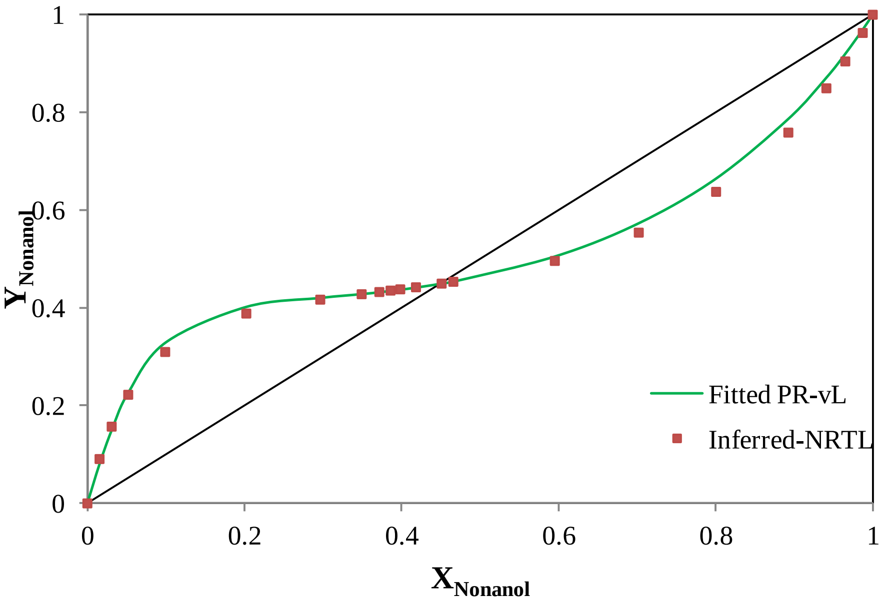

Figure 5-7: *xy* curve using the PR equation of state combined with a van Laar mixing rule for the 1-nonanol/1,3-propanediol system at P = 760 mmHg

Table 5-17 shows binary interaction parameters of different systems for different equations (i.e. k_{12} and k_{21} values).

Table 5-17: Binary interaction parameters of different binary mixtures for different equations of state

Mixture	PR-M		PR-vL		PRSV-M		PRSV-vL	
	k_{12}	**k_{21}**	**k_{12}**	**k_{21}**	**k_{12}**	**k_{21}**	**k_{12}**	**k_{21}**
Heptanol/Nonanol	-0.0211	-0.0037	-0.0100	-0.0542	-0.0181	-0.0173	-0.0236	-0.0096
Heptanol/Diol	-0.1440	-0.1362	-0.1370	-0.1374	-0.1442	-0.1456	-0.1452	-0.1472
Hexanol/Heptanol	0.0013	0.0207	0.0121	0.0555	0.0029	0.0168	0.0104	0.0334
Hexanol/Nonanol	-0.0167	-0.0451	-0.0907	-0.0130	-0.0140	-0.0520	-0.0800	-0.0156
Hexanol/Diol	-0.1573	-0.1750	-0.1689	-0.1352	-0.1615	-0.1854	-0.1748	-0.1386
Nonanol/Diol	-0.0381	-0.1411	-0.1536	-0.0562	-0.0369	-0.1442	-0.1527	-0.0630

5.5 Recommendations for Separation of Alcohols and Diols

As discussed, using the combination of PRSV EOS with the κ_1 values reported in Table 5-8 and a van Laar mixing rule results in a good correlation of the experimental VLE data for the six binary pairs studied in this work. Moreover, as the system containing 1-nonanol and 1,3-propanediol is highly the non-ideal, simple equations of state are not able to capture non-ideality. Therefore, a combination of a mixing rule with PRSV equation of state is strongly recommended. However, Table 5-16 shows that the best case for this non-ideal system is a combination of PR equation of state and a van Laar mixing rule.

6. Conclusions

The primary conclusion from this study is that the system containing 1-nonanol and 1,3-propanediol includes an azeotrope. Therefore, conventional distillation cannot be used to separate and/or purify all of the 1-hexanol, 1-heptanol, 1-nonanol and 1,3-propanediol. Some more specific conclusions coming out from this study are:

6.1 A New Method for Determining VLE Data of Mixtures

According to the potential shortcomings of using DSC for liquids in general, analyzing the sample temperature in lieu of the heat flow curve was evaluated in this work. The concept eliminated the two main shortcomings of using DSC for liquids: 1) effect of pre-evaporation; 2) discrepancy between the sample and the reference temperatures. Results for the boiling point of pure water as a function of pressure demonstrate that using DSC is a valid technique for determining boiling point of pure components. Also, the highly accurate results obtained for pure water indicate that dissolved gases do not have any effects on the results in this method at least to the desired accuracy in this study. As well, the obtained VLE data of three different well known binary mixtures shows that the method is also valid for accuratly determining boiling points of mixtures. Analyzing the temperature difference curve (i.e. temperature difference between the sample and the reference temperature) relies on the only reliable parameter in these experiments, the heating rate. Using first and second derivatives of the temperature difference curve can be used to find the boiling points of the mixtures accurately. In other words, the boiling point is the inflection point of the first derivative which is the minima on the second derivative curve. The location of this minima point on the second derivative curve was used in this study in order to locate the boiling points of mixtures. Therefore, the uncertainties, originating from pre-evaporation and temperature discrepancy between the sample and the reference temperatures in determining the onset value were overcome by evaluating the sample temperature. The major advantages of this technique are that the data collection is very fast (i.e. ~10 min/run) and quantity of sample required is very small (i.e. 5 μL/run).

6.2 VLE Data of Different Binary Pairs

The outlined method was used to determine the VLE behaviour of six different binary mixtures. Three linear alcohols (1-hexanol, 1-heptanol and 1-nonanol) as well as 1,3-propanediol, all by-products of a two step process for producting polyol monomer were studied in this work. The VLE data for the six different binary mixtures of the above components were studied at P = 1 atm. The experimental results showed that none of the binary pairs contains an azeotrope except for the 1-nonanol/1,3-propanediol system. Hence, conventional distillation is not capable of separating 1-nonanol and 1,3-propanediol to a purity of 98 wt%.

6.3 Thermodynamic Data Correlation

The experimental results for all six binary pairs were first correlated using different activity coefficient models including Margules, van Laar, Wilson and NRTL. Then, the Peng-Robinson (PR) equation of state, as well as the modified PR equation of state as proposed by Stryjek and Vera, combined with Margules and van Laar mixing rules were used to model the data. The Stryjek and Vera modified Peng-Robinson equation of state combined with a van Laar mixing rule can fit the data well. Therefore, this combination can be used for data correlation of linear alcohols and diols.

Bibliography

[1] Khoe, T. H., Otey, F. H. and Frankel, E. N. "Rigid urethane foams from hydroxymethylated linseed oil and polyol esters." *American Oil Chemists' Society* 49.11 (1972): 615-618.

[2] Guo, A., Demydov, D., Zhang, W. and Petrovic, Z. S. "Polyols and polyurethanes from hydroformylation of soybean oil" *Polymers and the Environment* 10.1 (2002): 49-52.

[3] Lyon, C. K., Garrett, V. H. and Frankel, E. N. "Rigid urethane foams from hydroxymethylated castor oil, safflower oil, oleic safflower oil, and polyol esters of castor acids." *American Oil Chemists' Society* 51.8 (1974): 331-334.

[4] Narine, S. S., Yue J. and Kong, X. "Production of polyols from canola oil and their chemical identification and physical properties." *American Oil Chemists' Society* 84.2 (2007): 173-179

[5] Mentzer, R. A., Greenkorn, R. and Chao, K. C. "Bubble pressures and vapor-liquid equilibria for four binary hydrocarbon mixtures." *Chemical Thermodynamics* 14.9 (1982): 817-830.

[6] Malanowski, S. "Experimental methods for vapour-liquid equilibria. Part I. Circulation methods." *Fluid Phase Equilibria* 8.2 (1982): 197-219.

[7] Malanowski, S. "Experimental methods for vapour-liquid equilibria. Part II. Dew-and bubble-point method." *Fluid Phase Equilibria* 9.3 (1982): 311-317.

[8] Watson, E. S. and O’Nail, M. J. "Differential microcalorimeter." *U.S. Patent No. 3,263,484.* 2 August (1966).

[9] Kohoutova, J.,Suska, J., Novak, J. P. and Pick, J. "Liquid-vapour equilibrium. XLV. System methanol-2-propanol-water." *Collection of Czechoslovak Chemical Communications* 35.11 (1970): 3210-3222.

[10] Verhoeve, L. and Schepper, H. D. "The vapor-Liquid equilibria of the binary, ternary and quaternary systems formed by acetone, methanol, propan-2-ol and water." *Applied Chemistry and Biotechnology* 23.8 (1973): 607-619.

[11] Arce, A. J., Martinez-Ageitos, J., Rodil, E. and Soto, A. "(Vapour+ liquid) equilibrium of (DIPE+ IPA+ water) at 101.32 kPa." *Chemical Thermodynamics* 35.6 (2003): 871-884.

[12] Brunjes, A. S. and Bogart, M. J. P. "Vapor-Liquid Equilibria for Commercially Important Systems of Organic Solvents: The Binary Systems Ethanol-n-Butanol, Acetone-Water and Isopropanol-Water." *Industrial and Engineering Chemistry* 35.2 (1943): 255-260.

[13] Myres, H. S. "Binary mixtures of naphtenes and aromatics- vapor-liquid equilibrium data." *Industrial and Engineering Chemistry* 48.6 (1956): 1104-1108.

[14] Delzenne, A. "Equilibre liquid-vapeur du systeme cyclohexane-toluene sous la pression atmospherique" *Bulletin De La Societe Chimique De France* 2 (1961): 295.

[15] Smith, J. C., Van Ness, H. C. and Abbott, M. M. "Introduction to chemical engineering thermodynamics." *McGraw-Hill Book Company*, New York (2005)

[16] Wankat, P. C. "Separations in chemical engineering: equilibrium staged separations." *Elsevier* New York (1988).

[17] Prausnitz, J. M., Lichtenthaler, R. N and de Azevedo, E. G. "Molecular thermodynamics of fluid-phase equilibria." *Prentice Hall* NJ (1998).

[18] Hala, E., Pick, J. and Fried, V. "Vapor-Liquid Equilibrium." *Pergamon Press* London (1968).

[19] Sayegh, S. G. and J. H. Vera. "Model-free methods for vapor-liquid equilibria calculations Binary systems." *Chemical Engineering Science* 35.11 (1980): 2247-2256.

[20] Ying H., Liu, H. and Prausnitz J. M. "A model-free method for calculating vapor-liquid equilibria for multicomponent systems from total-pressure or boiling-point data." *Fluid phase equilibria* 95 (1994): 73-92.

[21] Carveth, H. R. *Physical Chemistry* 3 (1899): 193.

[22] Sameshima, J. "On the system acetone-ethyl ether." *American Chemical Society* 40.10 (1918): 1482-1503.

[23] Chilton, T. H. *4th Symposium of Chemical Engineering Education* (1935): 64.

[24] Inglis, J. K. H. "The isothermal distillation of nitrogen and oxygen and of argon and oxygen." *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 11.65 (1906): 640-658.

[25] Tsiklis, D. S. "Handbook of techniques in high-pressure research and engineering." *Plenum Press* New York 504 P (1968).

[26] Conttrell, A. G. *American Chemical Society* 41 (1919): 721.

[27] Washburn, E. W. and Read J. W. "The laws of “concentrated” solutions. VI. The general boiling-point law." *American Chemical Society* 41.5 (1919): 729-741.

[28] Swietoslawski, W. and Romer, W. "Sur un nouvel appareil ebullioscopique" *Bull. Acad. Sci. Pol.* A (1924): 59-62.

[29] Swietoslawski, W. *Rocz Chem.*9 (1929): 266.

[30] Gillespie, D. T. C. "Vapor-liquid equilibrium still for miscible liquids." *Industrial & Engineering Chemistry Analytical Edition* 18.9 (1946): 575-577.

[31] Cailletet, L. "Sur la liquefaction de l'acetylene" *CR Acad. Sci.* 85 (1877): 851-852

[32] Kuenen, Dr. "On the condensation and the critical phenomena of mixtures of ethane and nitrous oxide." *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 40.243 (1895): 173-194.

[33] Sage, B. H., Schaafsma J. G. and Lacey W. N. "Phase Equilibria in Hydrocarbon Systems V. Pressure-Volume-Temperature Relations and Thermal Properties of Propane." *Industrial and Engineering Chemistry* 26.11 (1934): 1218-1224.

[34] Meskel-Lesavre, M., Richon D. and Renon H. "New variable volume cell for determining vapor-liquid equilibriums and saturated liquid molar volumes by the static method." *Industrial & Engineering Chemistry Fundamentals* 20.3 (1981): 284-289.

[35] Ratzsch, M.T., Kehlen, H. and Baumann, C. "Dew and bubble points for complex multi-component systems from pressure-volume measurement" *ZEITSCHRIFT FUR PHYSIKALISCHE CHEMIE-LEIPZIG.* 269.4 (1988): 785-793

[36] Malanowski, S. *Microfilm F 3.5*, CHISA-75 Cong. Prague (1975)

[37] Ammar, M. N. and Renon H. "The isothermal flash problem: new methods for phase split calculations." *AIChE journal* 33.6 (1987): 926-939.

[38] Chapman, W. G., Gubbins, K. E., Jackson, G. and Radosz, M. "SAFT: equation-of-state solution model for associating fluids." *Fluid Phase Equilibria* 52 (1989): 31-38.

[39] Heyen, G. "A cubic equation of state with extended range of application."*Chemical Engineering Thermodynamics, SA Newman* (1980): 175.

[40] Redlich, O. and J. Kwong N. S. "On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions." *Chemical Reviews* 44.1 (1949): 233-244.

[41] Fuller, G. G. "A modified Redlich-Kwong-Soave Equation of state capable of representing the liquid state." *Industrial and Engineering Chemistry Fundamentals* 15.4 (1976): 254-257.

[42] Peng, D. Y. and Robinson D. B. "A new two-constant equation of state." *Industrial and Engineering Chemistry Fundamentals* 15.1 (1976): 59-64.

[43] Stryjek, R. and Vera, J. H. "PRSV: An improved Peng-Robinson equation of state for pure compounds and mixtures." *Canadian Chemical Engineering* 64.2 (2009): 323-333.

[44] Valderrama, J. O. "The state of the cubic equations of state." *Industrial and Engineering Chemistry Research* 42.8 (2003): 1603-1618.

[45] Martin, J. J. "Cubic equations of state-Which?." *Industrial and Engineering Chemistry Fundamentals* 18.2 (1979): 81-97.

[46] Abbott, M. M. "Cubic equations of state." *AIChE* 19.3 (2004): 596-601.

[47] Carnahan, N. F. and Starling K. E. "Equation of state for nonattracting rigid spheres." *Chemical Physics* 51 (1969): 635.

[48] Boublík, T. "BACK equation of state for simple compounds." *Molecular Liquids* 134.1 (2007): 151-155.

[49] Wei, Y. S. and Sadus, R. J. "Calculation of the critical high pressure liquid-liquid phase equilibria of binary mixtures containing ammonia-Unlike interaction parameters for the Heilig-Franck equation of state." *Fluid Phase Equilibria* 101 (1994): 89-99.

[50] Sadus, R. J. "The Dieterici alternative to the van der Waals approach for equations of state: second virial coefficients." *Phys. Chem. Chem. Phys.* 4.6 (2002): 919-921.

[51] Sengers, J. V., Kayser, R. F., Peters, C. J. And White, H. J. "Equations of state for fluids and fluid mixtures." *International Union of Pure and Applied Chemistry (IUPAC)* NC: 2000.

[52] Nezbeda, I. "On molecular-based equations of state: rigor versus speculations." *Fluid Phase Equilibria* 182.1 (2001): 3-15.

[53] Wei, Y. S. and Sadus, R. J. "Equations of state for the calculation of fluid-phase equilibria." *AIChE* 46.1 (2004): 169-196.

[54] Deming, W. E. and Shupe, L. E. "The Beattie-Bridgeman equation of state and Bartlett's PVT data on a 3: 1 hydrogen-nitrogen mixture." *American Chemical Society* 53.3 (1931): 860-869.

[55] Benedict, M., Webb, G. B. and Rubin, L. C. "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures I. Methane, Ethane, Propane and n-Butane." *Chemical Physics* 8 (1940): 334.

[56] Benedict, M., Webb, G. B. and Rubin, L. C. "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures- Fugacities and Liquid-Vapor Equilibria." *Chemical Engineering Progress* 47.9 (1951): 449-454.

[57] Nishiumi, H. and Shozaburo, S. "An improved generalized BWR equation of state applicable to low reduced temperatures." *Chemical Engineering of Japan* 8.5 (1975): 356-360.

[58] Nishiumi, H. and Shozaburo, S. "Correlation of the binary interaction parameter of the modified generalized BWR equation of state." *Chemical Engineering of Japan* 10.3 (1977): 176-180.

[59] Nishiumi, H. "An improved generalized bwr equation of state with three polar parameters applicable to polar substances." *Chemical Engineering of Japan* 13.3 (1980): 178-183.

[60] Nishiumi, H. "Vapor-liquid equilibrium calculation of systems containing hydrogen by extended BWR equation of state." *Chemical Engineering of Japan* 16.6 (1983): 449-453.

[61] Strling, K. E. and Han M. S. "Thermo Data Refined for LPG (Part 14: Mixture)."*Hydrocarbon Processing* 51.5 (1972): 129.

[62] Anderko, A. "Equation-of-state methods for the modeling of phase equilibria." *Fluid Phase Equilibria* 61 (1990): 145.

[63] Kwak, T. Y. and Mansoori, G. A. "Van der Waals mixing rules for cubic equations of state. Applications for supercritical fluid extraction modelling."*Chemical Engineering Science* 41.5 (1986): 1303-1309.

[64] Trebble, M. A. and Bishnoi, P. R. "Extension of the Trebble-Bishnoi equation of state to fluid mixtures." *Fluid Phase Equilibria* 40.1 (1988): 1-21.

[65] Heyen, G. "A cubic equation of state with extended range of application."*Chemical Engineering Thermodynamics* (1980): 175.

[66] Huron, M. J. and Vidal, J. "New Mixing Rules In Simple Equations Of State For Representing Vapor-Liquid-Equilibria Of Strongly Non-ideal Mixtures." *Fluid Phase Equilibria* 3.4 (1979): 255-271.

[67] Solórzano-Zavala, M., Barragán-Aroche, F. and Bazúa, E. R. "Comparative study of mixing rules for cubic equations of state in the prediction of multicomponent vapor-liquid equilibria." *Fluid Phase Equilibria* 122.1 (1996): 99-116.

[68] White, W. B., Johnson, S. M. and Dantzig, G. B. "Chemical equilibrium in complex mixtures." *Chemical Physics* 28 (1958): 751.

[69] Gautam, R. and Seider, W. D. "Computation of phase and chemical equilibrium: Part I. Local and constrained minima in Gibbs free energy." *AIChE* 25.6 (1979): 991-999.

[70] Barker, J. A. "Determination of activity coefficients from total pressure measurements." *Australian Journal of Chemistry* 6.3 (1953): 207-210.

[71] Abbott, M. M. and van Ness, H. C. "Vapor-liquid equilibrium: Part III. Data reduction with precise expressions for GE." *AIChE* 21.1 (1975): 62-71.

[72] Margules, M. "Über die Zusammensetzung der gesättigten Dämpfe von Mischungen." *Sitzungsber Akad Wiss Wien* 104 (1895): 1243-1278.

[73] Wilson, G. M. "Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing." *American Chemical Society* 86.2 (1964): 127-130.

[74] Renon, Henri, and John M. Prausnitz. "Local compositions in thermodynamic excess functions for liquid mixtures." *AIChE* 14.1 (1968): 135-144.

[75] Abrams, D. S., and Prausnitz, J. M. "Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems." *AIChE* 21.1 (2004): 116-128.

[76] Alvarado, J. F. J. "Studies on phase equilibrium calculations from equations of state" *PhD Thesis Texas A&M University* Texas: (1993).

[77] Eubank, P. T., Lamonte, B. G. and Alvarado, JF J. "Consistency tests for binary VLE data." *Chemical and Engineering Data* 45.6 (2000): 1040-1048.

[78] Van Ness, H. C. "Thermodynamics in the treatment of vapor/liquid equilibrium (VLE) data." *Pure and Applied Chemistry* 67 (1995): 859-859.

[79] Tao, L. C. "General Equations for Testing Consistency of Multicomponent Vapor-Liquid Equilibrium Data." *Industrial and Engineering Chemistry Fundamentals* 1.2 (1962): 119-123.

[80] Tao, L. C. "New Methods of Testing Thermodynamic Consistency of Isobaric, Multicomponent Vapor-Liquid Equilibrium Data." *Industrial and Engineering Chemistry Fundamentals* 8.1 (1969): 133-137.

[81] Kojima, K., Hung M. M. and Ochi, K. "Thermodynamic consistency test of vapor-liquid equilibrium data:-Methanol∼ water, benzene∼ cyclohexane and ethyl methyl ketone∼ water." *Fluid Phase Equilibria* 56 (1990): 269-284.

[82] Moon, H. M., Kojima K. and Ochi, K. "Thermodynamic consistency test of vapor-liquid equilibrium data-alcohol-hydrocarbon systems." *Fluid Phase Equilibria* 62.1 (1991): 29-40.

[83] Biliaderis, C. G. "Differential scanning calorimetry in food research-A review." *Food Chemistry* 10.4 (1983): 239-265.

[84] Ladbrooke, B. D. and Chapman, D. "Thermal analysis of lipids, proteins and biological membranes. A review and summary of some recent studies."*Chemistry and Physics of Lipids* 3.4 (1969): 304.

[85] Bruylants, G., Wouters, J. and Michaux, C. "Differential scanning calorimetry in life science: thermodynamics, stability, molecular recognition and application in drug design." *Current Medicinal Chemistry* 12.17 (2005): 2011-2020.

[86] Fyans, R. L., Brennan W. P. and Earnest, C. M. "The evolution of differential scanning calorimetry: a review." *Thermochimica Acta* 92 (1985): 385-389.

[87] Höhne, G., Hemminger, W. F. and Flammersheim, H. J. "Differential scanning calorimetry." *Springer* New York (2003).

[88] Sauerbrunn, S., Crowe, B. and Reading, M. "Modulated differential scanning calorimetry." *American Laboratory* 24.12 (1992): 44-48.

[89] Cassel, B., Packer, R. and Shelton, C. T. "Modulated Temperature DSC and the DSC 8500: A Step Up in Performance." *Technical Note*, *Perkin Elmer Inc.* Shelton

[90] Gill, P. S. "Differential scanning calorimetry: recent applications." *Canadian Research and Development* 7 (1974): 23-26.

[91] Perrenot, B., de Valliere, P. and Widmann, G. "New pressure DSC cell and some applications." *Journal of Thermal Analysis and Calorimetry* 38.3 (1992): 381-390.

[92] Krawetz, A. A. and Tovrog, T. "Determination of Vapor Pressure by Differential Thermal Analysis." *Review of Scientific Instruments* 33.12 (1962): 1465-1466.

[93] Barrall, E. M., Porter, R. S. and Johnson, J. F. "Microboiling Point Determination at 30 to 760 Torr by Differential Thermal Analysis." *Analytical Chemistry* 37.8 (1965): 1053-1054.

[94] Kemme, H. R. and Kreps, S. I. "Vapor pressure determination by differential thermal analysis." *Analytical Chemistry* 41.13 (1969): 1869-1872.

[95] Seyler, R. J. "Parameters affecting the determination of vapor pressure by differential thermal methods." *Thermochimica Acta* 17.2 (1976): 129-136.

[96] Wiedemann, H. G. "Applications of thermogravimetry for vapor pressure determination." *Thermochimica Acta* 3.5 (1972): 355-366.

[97] Knudsen, M. "The molecular current of gases through openings and the effusion." *Annalen Der Physik* 28 (1909): 999-1016.

[98] Morie, G. P., Powers, T. A. and Glover, C. A. "Evaluation of thermal analysis equipment for the determination of vapor pressure and heat of vaporization." *Thermochimica Acta* 3.4 (1972): 259-269.

[99] Perkin-Elmer Corp. *Thermal Analysis Newsletter* 4. Norwalk (1967): 4-8.

[100] ASTM E 1782-08 "Standard test method for determining vapor pressure by thermal analysis." *ASTM* West Conshohocken (2008).

[101] Barrall, E. M. "Precise determination of melting and boiling points by differential thermal analysis and differential scanning calorimetry."*Thermochimica Acta* 5.4 (1973): 377-389.

[102] Tilinski, D. and Puderbach, H. "Experiences with the use of DSC in the determination of vapor pressure of organic compounds." *Thermal Analysis and Calorimetry* 35.2 (1989): 503-513.

[103] Jones, K. and Seyler, R. "Differential scanning calorimetry for boiling points and vapor pressure." *NATAS Notes* 26.2 (1994): 61-69.

[104] Contreras, M. D., Girela, F. and Parera, A. "The perfection of a method for the determination of the temperature/vapour-pressure function of liquids by differential scanning calorimetry." *Thermochimica Acta* 219 (1993): 167-172.

[105] Butrow, A. B. and Seyler, R. J. "Vapor pressure by DSC: extending ASTM E 1782 below 5 kPa." *Thermochimica Acta* 402.1 (2003): 145-152.

[106] Barrall, E. M., Porter R. S. and Johnson J. F. "Heats of Transition for Nematic Mesophases." *Physical Chemistry* 68.10 (1964): 2810-2813.

[107] Silva, L. Y. A., Falleiro, R. M. M., Meirelles, A. J. A. and Krahenbuhl, M. A. "Vapor–liquid equilibrium of fatty acid ethyl esters determined using DSC." *Thermochimica Acta* 512.1 (2011): 178-182.

[108] Casserino, M., Blevins, D. R. and Sanders R. N. "An improved method for measuring vapor pressure by DSC with automated pressure control."*Thermochimica Acta* 284.1 (1996): 145-152.

[109] Falleiro, R. M. M., Meirelles, A. J. A. and Krahenbuhl, M. A. "Experimental determination of the (vapor+ liquid) equilibrium data of binary mixtures of fatty acids by differential scanning calorimetry." *Chemical Thermodynamics* 42.1 (2010): 70-77.

[110] Wagner, W. and Pruss, A. "The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use." *Physical and Chemical Reference Data* 31.2 (2002): 387-536.

[111] Gmehling, J., Onken, U. and Arlt, W. "Vapor-liquid equilibrium data collection." *Dechema*, Frankfurt (1980).

[112] Stryjek, R. and Vera, J. H. "PRSV: An improved Peng-Robinson equation of state with new mixing rules for strongly nonideal mixtures." *Canadian Chemical Engineering* 64.2 (1986): 334-340.

[113] Wilhoit, R. C., and Zwolinski, B. J. "Physical and thermodynamic properties of aliphatic alcohols." *Physical Chemistry Reference Data* 2 (1973).

[114] Mokbel, I., Sawaya, T., Zanota, M. L., Naccoul, R. A., Jose, J. and de Bellefon, C. "Vapor-liquid equilibria of glycerol, 1,3-propanediol, glycerol +

water and glycerol + 1,3-propanediol." *Chemical and Engineering Data* 57 (2012): 284-289.

[115] Kemme, H. R. and Kreps, S. I. "Vapor pressure of primary n-alkyl chlorides and alcohols." *Chemical and Engineering Data* 14.1 (1969): 98-102.

[116] Rowley, R. L., Wilding, W. V., Oscarson, J. L. and Zundel, N. A. "DIPPR Data Compilation of Pure Compound Properties."*Design Institute for Physical Properties AIChE,* New York (2004).