Infinite Dilution Activity Coefficient Measurements for Limonene as a Green Solvent for Separation

By

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BTech in Chemical Engineering

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PREFACE

The study presented in this thesis was conducted in the Thermodynamic Research Laboratory, at the Durban University of Technology (DUT), Department of Chemical Engineering. This study was supervised by Dr Suresh Ramsuroop (DUT) and co-supervised by Dr Peterson Thokozani Ngema (DUT).

This thesis is presented as the full requirement for the degree of Master in Chemical Engineering. All the content presented in this thesis is original unless otherwise stated and has not been submitted previously to any tertiary institute as part of a degree.

B.P Mbatha (Candidate)

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I, Banzi Patrick Mbatha declare that:

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ii) This thesis has not been submitted for any degree or examination at any other university.

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Signed :_________________________	Signed:_
Dr S. Ramsuroop	Dr PT. Ngema

DECLARATION 2

Details of contribution to publications that form part and/or include research presented in this thesis (included publication in preparation, submitted, in press and published and gives details of contributions of each author to the experimental work and writing of each publication)

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ABSTRACT

There is an increasing call from the international communities for the replacement of traditional petrochemical solvents used by the chemical and allied industries in the separation processes. This has led to the new interest in finding alternative “green” solvents, which can be used to optimize the separation processes of non-ideal or close boiling mixtures for better separation.

This study focuses on investigating limonene as a “green” solvent to be utilized as a separating agent for separation processes. Limonene is a non-polar monoterpene solvent extracted from essential oils of the citrus peels. The extraction and distillation of this biomass extracted solvent releases fewer toxic pollutants and volatile gases, and as a result it has minimal impact to the environment. The infinite dilution activity coefficients (IDACs) for various solutes, which include alkanes, alkenes, alkynes, cycloalkanes, heterocycles, alcohol, aromatics, ketones, ethers, nitrile and water in the limonene solvent were measured using gas-liquid chromatography at (303.15, 313.15, 323.15 and 333.15) K. Through the experimental infinite dilution activity coefficients (IDACs), the values of partial molar excess enthalpy at infinite were obtained using the Gibbs-Helmholtz equation. To evaluate its potential of limonene as a mass transfer separation agent, its selectivity and capacity were calculated from the experimental limiting activity coefficients and were compared with ionic liquids and conventional solvents.

From the results of this study, it was generally observed that for all solutes the activity coefficient at infinite dilution decreased with the increase of temperature and increased with the increase of alkyl chain length of the solute. The triple bond alkyl solutes had a strong interaction with the limonene, due to their low values of activity coefficients at infinite dilution.

In some selective test cases, the selectivity and capacity for the separation of hexane/hex-1-ene and ethanol/water showing promising results when compared with ILs. The selectivity and capacity for the separation mixture of heptane/benzene, octane/ethylactetate, heptane/pyridine, octane/pyridine, and octane/thiophene indicated that the limonene was not suitable as the extraction solvent when compared with other ILs and conventional solvents. However, more investigation of limonene must be conducted through measurements liquid-liquid equilibrium and vapour-liquid equilibrium. Such data would provide useful information and understanding into the separation of hexane/hex-1-ene and ethanol/water mixtures. Green solvents extracted from biomass which have high boiling temperatures also be studied and compared with limonene solvent.

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NOMENCLATURE

A	Parameter (regressed) in the extended Antoine vapor pressure equation
B	Parameter (regressed) in the extended Antoine vapor pressure equation
B_{i1}	Second virial coefficient of the solute [$m^3.mol^{-1}$]
B_{i2}	Mixed second virial coefficient of the solute [$m^3.mol^{-1}$]
C	Parameter (regressed) in the extended Antoine vapour pressure equation
C_L	Concentration of solute in liquid phase [$mol.m^{-3}$]
C_M	Concentration of solute in mobile phase [$mol.m^{-3}$]
$\widehat{f_i}$	Fugacity of component i in solution [kPa]
f_i	Fugacity of pure component i [kPa]
H^E	Partial molar excess enthalpies at infinite [$kJ.mol^{-1}$]
I_c	Criticlal ionaisation potential, [$kJ.mol^{-1}$]
J_2^3	Pressure correction term
$K_{j,s}^{\infty}$	Capacity at infinite dilution of solvent (s)
K_L	Partitioning coefficient
n	Number of carbon atoms
n_3	Number of moles of solvent in the column
P	Total pressure [Pa]
p_1	Partial vapor pressure [Pa]
P_c	Critical pressure [Pa]
P_i	Inlet pressure [Pa]
p_i^o or P_i^*	Saturated vapor pressure [Pa]
P_o	Outlet (atmospheric) pressure [Pa]

p_w^o	Saturation vapor pressure of water
R	Universal gas constant [J.mol.$^{-1}$.K^{-1}]
$S_{ij,s}^{\infty}$	Selectivity at infinite dilution of component (*i*) over component (*j*), in solvent
T	Absolute temperature [K]
T_c	Critical temperature [K]
T_f	Temperature of the flow meter [K]
t_G	Retention time of an inert chemical (helium) [s]
t_r	Retention time of the solute [s]
U	Flow rate [m^3.s^{-1}]
U_o	Corrected flow rate of helium gas [m^3.s^{-1}]
V	Volume [m^3]
V_c	Critical molar volume [cm^3.mol^{-1}]
V_G	Gas phase volume [m^3]
v_i	Liquid molar volume of pure solute [cm^3.mol^{-1}]
v_i^{∞}	Partial molar volume of the solute [cm^3.mol^{-1}]
V_L	Liquid phase volume [m^3]
V_N	Net retention volume [m^3]
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in gas phase

Greek letters

γ_{13}^{∞}	Infinite dilution activity coefficient
γ_i	Activity coefficient of each species in a solution
a_i	Activity
μ	Chemical potential
ρ	Density

Subscript

f	Bubble flow meter
G	Gas phase
i	Property related to pure component
ij	Interaction properties
j	Component
o	Outlet
r	Reduce property

Superscript

L	Liquid phase
M	Mobile phase
o	Outlet
exp	Experimentally determined
lit	Literature

Abbreviations

CFC	Chlorofluorocarbon
DES	Deep eutectic solvent
DB	Dichlorobenzene
EQ	Equivalent
EXP	Experimental
Fe	Iron
GC	Gas chromatography
GLC	Gas liquid chromatography
IDAC	Infinite dilution activity coefficient
IL	Ionic liquid
LCD	Liquid crystal display
LIT	Literature
LLE	Liquid-liquid equilibrium
NADES	Natural deep eutectic solvent
N	Nitrogen
NMVOC	Non-methane volatile organic compound
NRTL	Non-Random Two Liquid
P	Phosphorous
R.D	Relative Deviation
TCD	Thermal conductivity detector
UNIQUAC	Universal quasichemical
VLE	Vapour-liquid equilibrium
VOC	Volatile organic compound

CHAPTER 1

INTRODUCTION

The need to replace volatile organic compounds (VOCs) by benign solvents in industrial applications is seen as a key requirement in developing more sustainable processes. The petrochemical solvents which are normally called traditional solvents have been widely used in the chemical industry for several years. These solvents are consumed in large quantities due to their availability and low cost. These petrochemical solvents which are generally obtained via energy intensive separation process, can account for more than 50% of the energy costs (Sholl and Lively, 2016). These traditional solvents which generally produce volatile gases, adversely affect the environment by polluting the environment, depleting the ozone layer, posing risks to human health, and are a non-renewable resource (Wan et al., 1995, Hanmoungjai et al., 2000). The environmental, sustainability, and health and safety issues relating to these traditional solvents have driven the research on developing alternative environmentally friendly solvent processes/systems to replace the use of traditional volatile organics. Some of the alternatives to the traditional solvents that has received extensive attention include ionic liquids (ILs), deep eutectic solvents (DESs), and natural deep eutectic solvents (NADESs). Solvents derived from renewable biological feedstocks that are non-toxic and biodegradable are becoming highly desirable replacement for petrochemical solvents. Whilst these have been identified as potential alternative solvents to VOCs in a wide variety of industrial separation applications, the reduced cost, complexity and environmental impact of large-scale industrial manufacture of the alternative solvents is a necessary precursor for its use (Xu et al., 2015).

D-Limonene ((+)-limonene) is the R enantiomer of 1-methyl4-(1-methylethenyl)-cyclohexene and is a naturally occurring cyclic monoterpene having the molecular formula $C_{10}H_{16}$. Limonene, a solvent derived from renewable biological feedstock, has been identified as a potential alternative to the traditional solvent due to its biodegradability and low toxicity (Mamidipally and Liu, 2004, Liu and Mamidipally, 2005, Virot et al., 2008) and its performance as cleaning and degreasing solvent (Toplisek and Gustafson, 1995). It is the main component of essential oil extracted from a range of citrus vegetation and is distilled as a clear, colour-less, natural hydrocarbon liquid for technical, pharmaceutical and food-based uses (Ciriminna et al., 2014). Furthermore, the extraction and distillation of limonene releases fewer toxic pollutants and volatile gases, as a result it has minimal impact to the environment (Pourbafrani et al., 2013). Due to its flavour and fragrance, it’s widely used in cosmetics, pharmaceuticals, natural medicine, and in the food industry (Uemura et al., 1997a).

Activity coefficients at infinite dilution (γ_{13}^{∞}) provides incisive information concerning solute–solvent interactions by characterising the intermolecular interaction behaviour of a solute molecule surrounded by the solvent. The activity coefficients at infinite dilution presents a better knowledge of the phase equilibrium of high purity separation processes. This data is often used by engineers for the synthesis, design, and optimization of separation processes of complex mixtures such as close boiling mixtures and mixtures exhibiting azeotropes or limited miscibility. Activity coefficient provides useful information for solvent screening purposes for extractive distillation or liquid-liquid extraction and for evaluating alternative processes in the cases where it is not feasible to use normal distillation.

The gas liquid chromatography (GLC) method is used to determine the activity coefficients of solutes, whereby the inner part of the chromatic column is coated with the solvent and solutes are introduced with the carrier gas (Nkosi et al., 2019, Smith et al., 2001, Letcher et al., 2003, Deenadayalu et al., 2005). The retention times for the solutes in the stationary solvent represent the strength of interaction of the solute in the solvent. Direct from the experimental values of γ_{13}^{∞}, the selectivity and capacity factors can be calculated and it provide critical information on the separation performance of the solvent for separation processes. High value of selectivity will result on the distillation with low number of equilibrium stages. The capacity is inversely proportion to the amount of solvent used for extraction, hence the lower the capacity the higher the amount of solvent required for extraction.

Aim of the study

This project aims to identify and evaluate potential green solvents to replace traditional extractive petrochemical solvents that have been widely used in chemical industries for separation processes. The traditional solvents are a non-renewable resource, and they cause a negative impact on the environment. Green solvents are environmentally friendly because they are generally non-toxic, biodegradable and they are sustainable renewable resources. Specifically, the aim of this research will focus on evaluating limonene as a green solvent for industrial separation processes such as liquid-liquid extraction and extractive/azeotropic distillation processes.

Objectives of the study

The objectives are:

- Investigate the solvency properties of limonene and assess its potential as a green solvent.
- Evaluate its application as an extractive solvent for the separation of non-ideal systems (close boiling point and azeotropic systems).
- To calculate the selectivity and capacity of limonene and rank its performance against traditional petrochemical solvents used in industrial separation processes
- To generate new data since there is no published data on this study for the measurements for infinite dilution activity coefficient of limonene –solute systems.

Dissertation outline

- Chapter 1 : Provides the introduction to the study and outlines the project objectives.
- Chapter 2 : Presents the literature review of the previous scientific work done related to infinity dilution activity coefficients.
- Chapter 3 : Provide details of the thermodynamics framework and relevant calculations related to this project.
- Chapter 4 : Outline the review of experimental techniques and equipment.
- Chapter 5 : Presents the experimental equipment and procedures used in this study.
- Chapter 6 : Presents the results of the infinite dilution activity coefficients for the test system and the experimental work and the discussion of the experimental results.
- Chapter 7 : Presents conclusion and recommendations for future works.

In this study, limonene is evaluated as potential solvent for separation processes. There is limited experimental data found in the literature for infinite dilution activity coefficients (IDAC) for limonene. The performance of limonene is compared with ionic liquids (ILs) solvents for selected non-ideal separation cases where the IL was a recommended solvent. In this study, the separation mixtures such hexane/hexene, heptane/benzene, ethanol/water, octane/ethylactetate, octane/acetonitrile, octane/thiophene, heptane/pyridine and octane/pyridine were considered.

CHAPTER 2

LITERATURE REVIEW

Chapter overview

This chapter provides a history of green chemistry and its concept. Highlighting the principles of green chemistry, and the development of green solvents. The extraction and physical properties of limonene and its application as a green solvent in the separation processes. This chapter also provides the use of gas liquid chromatography for the determination of infinite dilution activity coefficient values.

2.1. Green chemistry

The use of traditional solvents such as benzene, toluene and xylene by the chemical industries in the separation process has been an issue of great environmental concern. These solvents are characterized by high volatility and it is estimated that about 20 million tons per year of volatile organic compounds are released into the atmosphere (Brennecke and Maginn, 2001), causing air pollution, global climate changes and human health issues (Sheldon, 2001).

The concept of green chemistry was established in the early 1990s (Abbott, 1986, Alessi et al., 1991) to design safer chemical products and processes for a sustainable future (Anastas and Warner, 1998). It is considered as the new way of thinking that has the potential to contribute towards sustainable development (Lancaster, 2002, Wardencki et al., 2005). It is described as pro-active and innovative science, targeting at pollution prevention and waste minimization. In simple terms, it is 'cleaner, cheap and smarter chemistry' (National Environment Health Association., 1997) which indicates that chemistry can be done in a way that does not cause any harm to the human health and environment. It is defined as "the design, manufacture and application of chemical products and processes to reduce or to terminate the use and generation of hazardous waste" (Anastas and Warner, 1998).

The "Twelve principles of green chemistry" were formulated by Anastas and Warner in 1998, to give guidance for the application of sustainable thinking with regards to the practice of chemistry. The principles of green chemistry are to give encouragement to the chemists to consider the environmental impact of chemicals and manufacturing as early as possible in the discovery process.

The twelve principles are:

1. It is better to prevent waste than to treat or clean up waste after it has been created.
2. Synthesis methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, the synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. The use of auxiliary substances (e.g. solvents, separating agents) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically possible.
8. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
9. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

2.2. Green solvents

The solvent sector is mostly dominated by petroleum-derived products (Clark et al., 2015). In the transition to a green economy, the implementation of sustainable solvents has a potential cause of a significant impact across the industrial landscape. Based on the twelve green chemistry principles, green solvents are the ones that are sustainable and safe throughout its life cycle, clean manufacturing from renewable materials, easy to recover and recycle (Capello et al., 2007). Environmental toxicity has been identified as a key factor when selecting the solvent. Solvents should be minimally toxic to human health and the environment, and should not pollute the environment (DeVito, 1996). The consideration for what constitutes a safe solvent might be summarized as follows:

- It must have reduced human and environmental absorption.
- Its environmental toxicity should be understood.
- Its environmental fate is understood.

In the chemical processes, the ideal or the greenest option is to completely eliminate the use of the solvent when designing processes. However, it is impossible or impractical to completely avoid the use of a solvent (DeSimone, 2002). The fifth and seventh principles of green chemistry provides the bases of the alternative use of green solvents. It was estimated that by 2020, the green solvent market will be worth $ 8 billion (Kumar Sahu, 2016).

Even though the biomass is highly abundant and constantly generated on the planet, the concerns of exploitation and sustainability risks cannot be ignored. The supply and demand are highly debated since it competes with the food production, in terms of the land use and market price as occurred in the infamous case of biodiesel (Sheppard et al., 2011). The strategy to minimize these issues has been proved by the exploitation of food and agricultural waste as to source bio-solvents (Pfaltzgraff et al., 2013). Naturally derived terpenes are the most feasible alternative solvent for the replacement of traditional petrochemical solvents and they are recognized as environmentally safer. In this study limonene is used as a “green solvent”.

Terpenes are classified as unsaturated hydrocarbon, which is made up of isoprene C5 units and is found in the essential oils and oleoresin of plants such as conifers (Chemat et al., 2012a). Terpenes are considered to be the largest classes of renewable chemical compounds produced in nature (Schwab et al., 2013). Most of the terpenes are acyclic, bicyclic or monocyclic and differ slightly in physical properties.

2.3. Limonene

Limonene is a monoterpene hydrocarbon which has a wide range application in the chemical industry. It is the main component of essential oil extracted from the rinds of the citrus fruits and it is therefore a by-product of the fruit juice industry. It can be obtained through natural methods such as steam distillation of citrus peels. With a production of more than 50 million tons, the orange juice industry provides an important source for limonene and the research for the valorization of waste and by-products. The U.S. Food and Drug Administration has considered the limonene as a GRAS (Generally Recognized as Safe) material for use in the food and pharmaceutical industries as flavours and fragrances (Mira et al., 1999); (Guenther, 1952).

Physical properties of limonene vs tradition solvent

Limonene (4-isopropenyl-1-methylcyclohexene) is a colourless or pale-yellow liquid monoterpene hydrocarbon as shown in Figure 2- 1, with a molar mass of 136.23 g/mol (Schwab et al., 2013). It is characterized by a citrus smell or pine smell. The limonene occurs in the peels of the citrus fruits, such as sweet orange, tangerine, lemon and lime (Chhikara et al., 2018). Limonene is soluble in hydrocarbons and alcohols except with methanol and water in which it is partially miscible (Tamura et al., 2009).

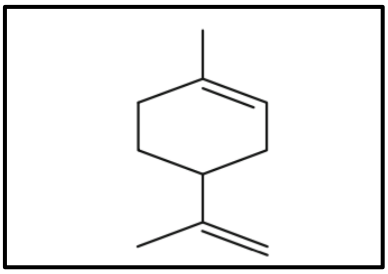


Figure 2- 1: Chemical structure of limonene (SigmaAldrich, 2020).

The comparison between limonene and toluene (a typical petrochemical solvent) concerning the physical properties are listed in Table 2- 1 and the similarities between the solvents are observed (SigmaAldrich, 2020).

Table 2- 1: Physical properties of limonene and toluene (SigmaAldrich, 2020).

Property	Limonene	Toluene
Molecular weight (MW) - g/mol	136.24	92.14
Density (d) - g/cm^3	0.841	0.87
Molar volume (V_m) - cm^3/mol	161.9	106.3
Viscosity (η)- cP (25°C)	0.90	0.56
Boiling point (b.p.) - °C	176	110
Melting point (m.p.) - °C	-74	-93
Flash point (f.p.) - °C	50	4
Dipole moment (D) - D	0.29	0.31
Vapour pressure (P_v) - mmHg (20 °C)	2.0	22

The evidence from Table 2- 2 suggests that the toluene possesses more risk and causing long term damage to organs under prolonged exposure (Campo et al., 2009). The limonene shows low flammability hazards and overall lower health impact, indicating that it is a safer replacement to toluene. The skin sensation and higher aquatic toxicity must be considered when profiling limonene (Paggiola, 2016).

Table 2- 2: Comparison of GHS phrases related to Environment Health & Safety profile (Campo et al., 2009).

Limonene	Toluene
H226 Flammable liquid and vapour.	H225 Highly flammable liquid and vapour.
H304 May be fatal if swallowed and enters the airways.	**H304** May be fatal if swallowed and enters the airways.
H315 Causes skin irritation.	**H315** Causes skin irritation.
H317 May cause allergic skin Reaction.	**H336** May cause drowsiness or dizziness.
	H362d Suspected of damaging the unborn child.
	H373 May cause damage to organs through prolonged exposure.

Life-cycle assessment

The study of life-cycle assessment (LCA) was conducted by the industry to evaluate the impact of limonene compare to toluene (Roberts, 2012). Table 2- 3 shows that toluene has potential to cause climate change eight times higher than the limonene. While limonene shows the favourable profile and the encouraging results, however more alternative ways of producing limonene and toluene may be assessed for more a favourable profile.

Table 2- 3: Comparison of life-cycle impact data for limonene and toluene (Roberts, 2012).

Criteria - Unit	Limonene	Toluene
Climate change - kg CO_2 eq	207	1654
Water depletion - m^3	0.75	1.03
Metal depletion - kg Fe eq	0.371	0.892
Fossil depletion - kg oil eq	52	1526
Terrestrial acidification - kg SO_2 eq	0.83	4.25
Fresh water eutrophication - kg P eq	4.84E-02	6.87E-03
Marine eutrophication - kg N eq	0.28	1.22
Terrestrial ecotoxicity - kg 1,4-DB eq	0.006	0.016
Fresh water ecotoxicity - kg 1,4-DB eq	0.468	0.86
Marine ecotoxicity - kg 1,4-DB eq	0.54	0.99
Human toxicity - kg 1,4-DB eq	49.97	90.23
Ozone depletion - kg CFC-11 eq	9.42E-06	8.28E-08
Photochemical oxidant formation - NMVOC	0.81	5.57

2.4. Applications for limonene as a solvent

The limonene solvent has been identified as a potential alternative to the traditional solvent due to its biodegradability and low toxicity (Mamidipally and Liu, 2004, Liu and Mamidipally, 2005, Virot et al., 2008). Thus far, limonene has been studied in a wide range of applications related to the chemical industry and these include:

- It is used in cosmetics, medicine (including aromatherapy in natural medicine for relaxing, harmonizing and stabilization of the nervous system), perfume industry and the food industry (Flavour and fragrant additives for food). It is also present in the carbonated beverages such as Coca-Cola, in fruit juice, ice creams and sweets (Uemura et al., 1997b).
- Agriculture as an ecological insecticide and as a part of feeds for poultry due to its antibacterial and disinfecting properties (Ciriminna et al., 2014).

- Serve as an alternative solvent for chlorinated compounds in the production process for the aviation, electronics and automotive industry (Keinan et al., 2005).
- It forms an environmentally friendly aqueous cleaning solution with low flammability and with the potential of removing dirt in concretes, general duty ship maintenance, degreasing diesel engines and bearings (Martin-Luengo et al., 2010).
- Replacement for n-hexane in the microwave extraction of oils from olives (Byrne et al., 2004).
- Medically it is a good solvent for cholesterol and also in clinical treating of the removal of gallstones (Bähr et al., 2012).

Limonene as an alternative solvent for Soxhlet Extraction

The soxhlet has been used for many years as a technique for the recovery of fats and oils from bio-feedstock. However, the challenges with soxhlet were the long hours of extraction, energy consumption and the use of a traditional solvent such as n-hexane (Johnson and Lusas, 1983). New extraction system called microwave-assisted soxhlet was developed using a green approach, whereby 90% of the solvent is recycled and extraction time reduced from 8 hours to 32 minutes (Virot et al., 2007); (Virot et al., 2008). Virot et al. (2008) proposed a combination of microwave-assisted soxhlet and limonene solvent, and this step was followed by a microwave assisted distillation using a clevenger system as shown in Figure 2- 2.

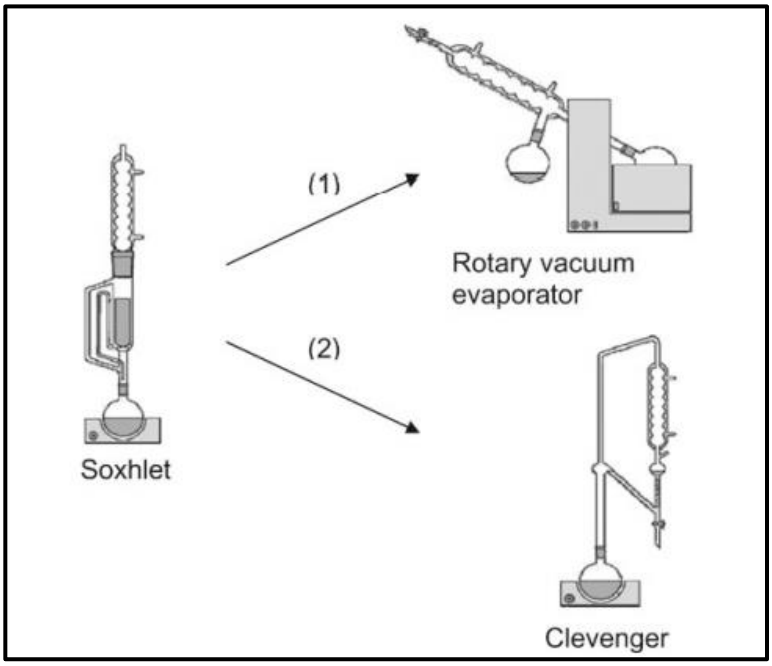


Figure 2- 2: Soxhlet extraction system (1) n-hexane and (2) limonene (Virot et al., 2008).

Limonene as an alternative solvent for Dean-Stark distillation

The determination of moisture in the food analysis is a key factor when selecting a suitable drying method. Wide range of distillation-based methods have been tested (Chemat et al., 2012b). Dean and Stark developed the first continuous and refluxing method (Dean and Stark, 1920) and as result, the method became the reference for the determination of water in the food products containing volatile compounds (Balladin and Headley, 1999). Toluene has been used as a solvent on the Dean and Stark method. However, due to its toxicity to the environment and human health, limonene was used to replace the toluene (Veillet et al., 2009). The dean-stark method as shown in Figure 2- 3, was based on the ability for the solvent to form the azeotropic mixture with water confined in the food matrix.

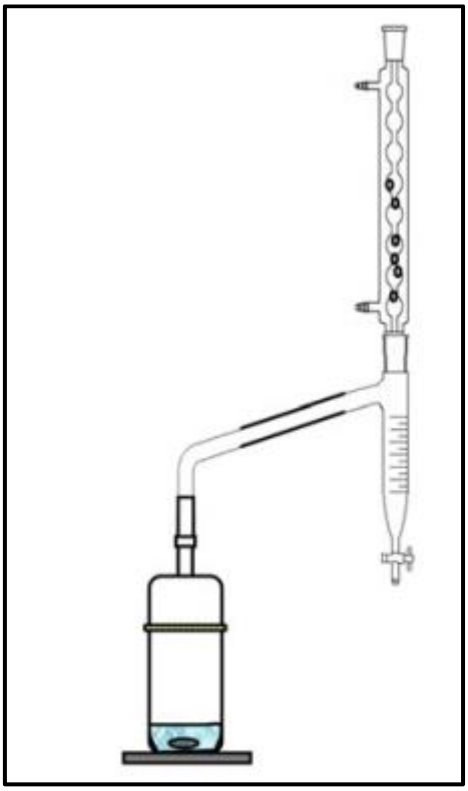


Figure 2- 3: Dean-stark apparatus (Dean and Stark, 1920).

Limonene as an alternative solvent for extraction of by-products

The extraction of lycopene from the tomato by using dichloromethane has been used for many years. The lycopene is used in food dye. The conventional method for extraction of lycopene uses large volumes of organic solvents which are toxic and hazardous to the environment and human health. The limonene was used as an alternative for dichloromethane solvent in the extraction of lycopene (Chemat-Djenni et al., 2010), due to its low toxicity and that it is recognized as a GRAS agent.

2.5. Types of separation processes that use mass separating agents.

Azeotropic distillation

In the azeotropic distillation, the entrainer forming a new azeotrope with the components of the azeotropic mixture is added to affect the desired separation. The formation of the single liquid phase through the addition of the entrainer and usable without further separation, is referred to as the homogeneous azeotropic distillation (Seader and Henley, 2006). In the cases whereby two liquid phases are formed and separated by decanter into organic and aqueous liquid phases, it is referred as heterogeneous azeotropic distillation. The schematic diagram of the azeotropic distillation is presented in Figure 2- 4. The heterogeneous azeotropic distillation has more advantages as compared to the homogeneous due to its industrial preference. In the azeotropic distillation, the solvent is vapourised at the top of the column, as a results, large amount of energy is consumed (Vane et al., 2010).

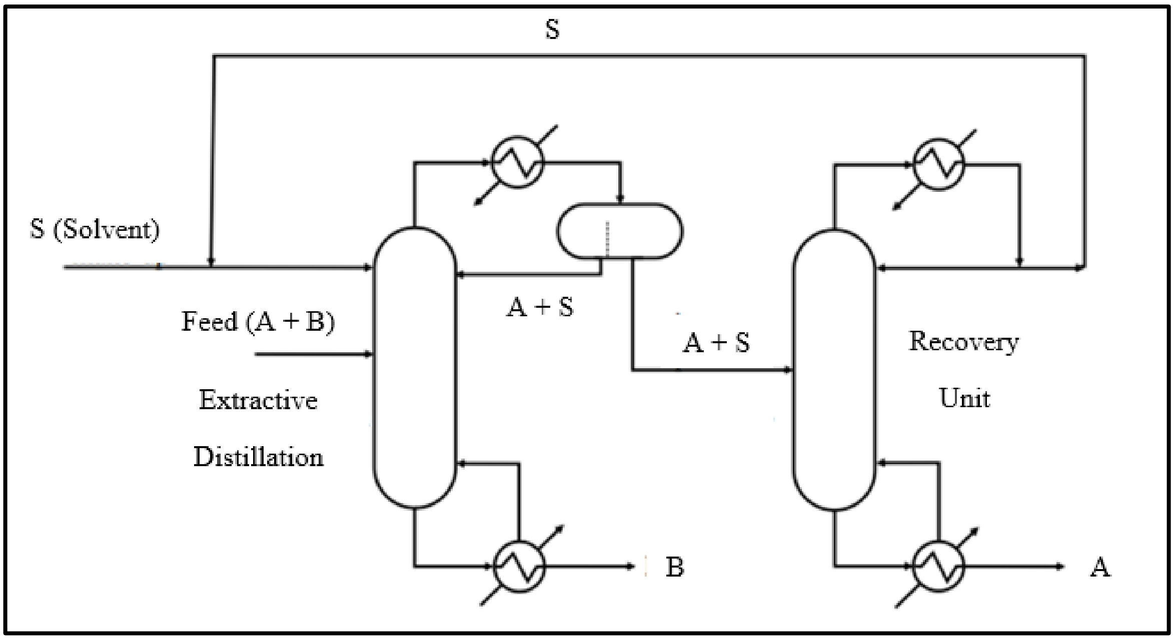


Figure 2- 4: Schematic diagram of the azeotropic distillation (Huang et al., 2010).

A- Carrier; B- Solute; S- Solvent

Extractive distillation

The extractive distillation uses a solvent with a boiling point higher than that of the azeotropic mixture and it is widely used in the petrochemical industry. The solvent which is added into the azeotropic feed mixture as to change the relative volatility by forming the affinity with one of the components (Gil et al., 2014). High purity of distillates is obtained from each of the columns and the solvent is recovered as the bottom product and recycled back into the extractive column for reuse (Lei et al., 2003) as shown in Figure 2- 5. The extractive distillation is more advantageous than the azeotropic distillation. The extractive distillation is referred to as a partial vapourization process, hence it consumes less energy (Bastidas et al., 2010).

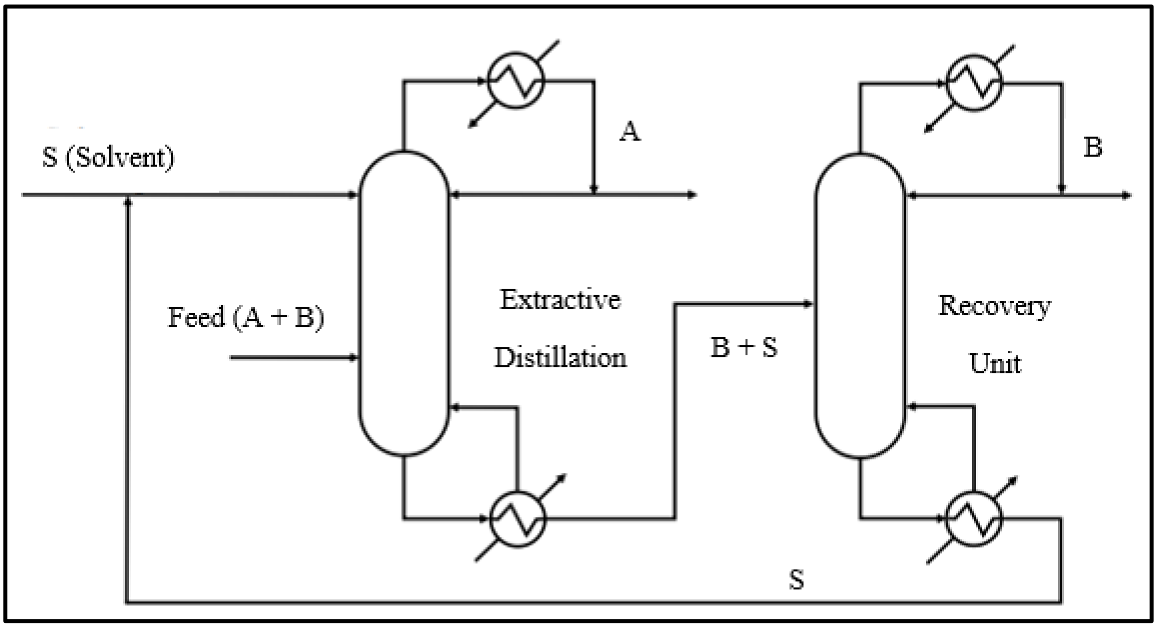


Figure 2- 5: Schematic diagram of the extractive distillation (Lei et al., 2003)

A- Carrier; B- Solute; S- Solvent

Liquid-liquid extraction

Liquid-liquid extraction (LLE), sometimes called solvent extraction, is a separation of components int the liquid mixture by contact with the insoluble liquid. It is ranked second in importance to distillation and it belongs to the category of countercurrent and diffusional separation processes (Pratt, 1983). The LLE consists of four elements namely: feed, solvent, raffinate and extract as shown in Figure 2- 6 (Dadgar, 1986).

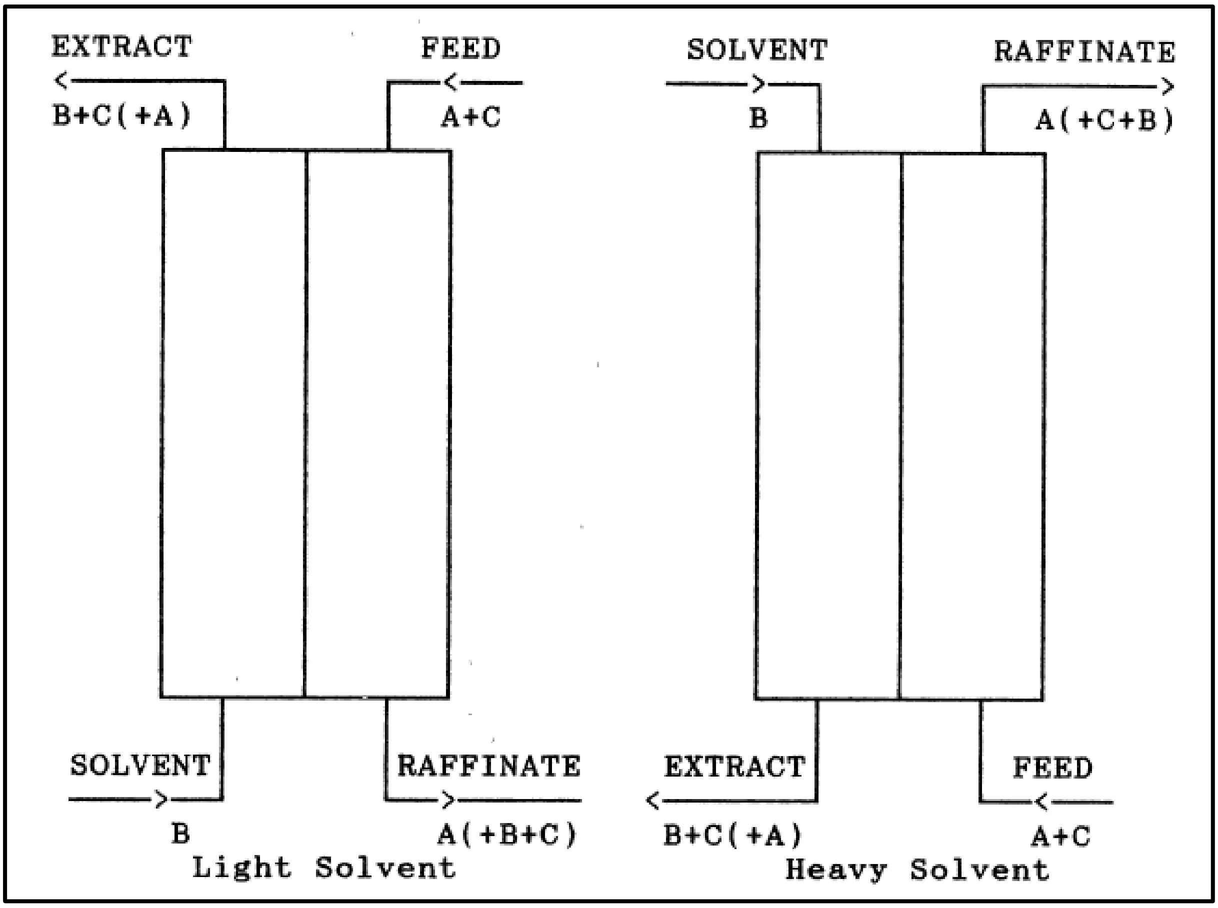


Figure 2- 6: Schematic diagram of the Liquid-liquid extraction (Dadgar, 1986).

A- Carrier; B- Solvent; C- Solute (Distributed Component)

Advantages of LLE

Extraction is preferred to distillation for the following (Seader and Henley, 2006):

- Extraction of small quantities of components such as hormones in animal oils.
- In situations of dissolved or complex inorganic substances in aqueous organic substances.
- Recovery of heat sensitive materials, where extraction may be less expensive than vacuum distillation.
- Separation of the mixture according to the type of chemical instead of relative volatility.
- Separation of close boiling point components where solubility can be exploited.
- Separation of azeotropes.

Disadvantages of LLE

- The need for the solvent increases the complexity and the cost of the column.
- If chemicals are miscible, distillation columns may be needed to recover the solvent from the raffinate.

Phase Equilibria Data

The phase equilibria data such as VLE, LLE and SLE provides an important source of information on fluid properties when designing the industrial separation equipment. The separation processes are costly, hence the data from which they designed needs to be accurate to optimise the design. Phase equilibrium data can be experimentally measured, predicted or derived from critically measured properties.

Phase equilibria data of D-limonene

The Isobaric binary vapor−liquid equilibrium (VLE) data were measured for the 1-methyl-4-(1-methylethenyl)-cyclohexene (D-limonene) + (ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, or hexan-1-ol) systems at lower pressure of 40kPa (Ngema et al., 2012). The experimental data was regenerated using the nonrandom two-liquid (NRTL) and Wilson activity coefficient models. It was found the system of 1-methyl-4-(1-methylethenyl)-cyclohexene + (butan-1-ol or pentan-1-ol or hexan-1-ol) exhibits minimum temperature azeotrope. The system of 1-methyl-4-(1-methylethenyl)- cyclohexene + ({ethanol or propan-1-ol or propan-2-ol) exhibited largest positive deviation from Raoult’s law with no azeotropic behaviour.

Organic solvents such as trichloroethane and trichloroethylene have been used traditionally to reduce the volume of styrene-foam. It was reported that limonene worked effectively on volume reduction of styrene-foam (Kodama et al., 2003). The vapour-liquid equilibrium data were measured for the system of ethanol + limonene and 1-propanol + limonene at the atmospheric pressure. The results obtained were correlated by the Wilson equation.

The equilibrium data for the experimental liquid-liquid equilibrium of the limonene + ethanol + water system was measured at the temperature of 239.15, 303.15, 313.15 and 323.15 K (Cháfer et al., 2004). The equilibrium data were presented and correlated using NRTL and UNIQUAC equations. The models were tested through the comparison with the experimental results to ensure reliability.

The binary mixture of (methanol + limonene) and the liquid-liquid equilibrium (tie-lines) for the ternary mixture (methanol + ethanol + limonene) have been measured at the temperatures of (288.15, 298.15 and 308.15) K (Tamura et al., 2009). The experimental results were found to be accurate and modified and compared with the UNIQUAC model. The temperature dependence of binary and ternary liquid-liquid equilibrium for the binary (methanol + limonene) and ternary (methanol + ethanol + limonene) mixtures was calculated successfully using the extended and modified UNIQUAC model.

Solvent selection in separation processes

When selecting the solvent for any separation process, the following criteria must be used to ensure the safety and efficiency of the operation (Lei et al., 2005):

- Cheap and easily accessible.
- High selectivity and capacity.
- Miscible with the feed and no separation required at the regeneration step.
- High chemical and thermal stability.
- Negligible corrosivity
- Low toxicity
- Low viscosity

2.6. Infinite dilution activity coefficient

The infinite dilution activity coefficient is defined as the limiting value of the activity coefficient of the solute when its concentration approaches zero (Seader et al., 2011). It is used to account for the deviation of real solutions from ideal solutions. The infinite dilution activity coefficient can guide on selecting the potential solvent for particular separation processes and it can be used to design commercial separation processes. The infinite dilution activity coefficients and partition coefficients values provide important information on the intermolecular interaction between limonene solvent and solutes. These values are used to calculate the partial molar excess enthalpies at infinite dilution, selectivities and capacity of the solvent, and the equation are explained in chapter three.

The temperature dependence of the activity coefficient can be used to calculate the partial molar excess enthalpies at infinite by using Gibbs-Helmholtz Equation. These selectivity and capacity play a vital role in the separation of high purity chemicals. The infinite dilution activity coefficient values are required to select the solvent for separation processes and to check separation problems such as azeotropes, close-boiling points and miscibility gaps, aiding in the design of various separation units (Smith et al., 2001).

The relevant thermodynamic framework for infinite dilution activity coefficients is presented in Chapter 3

Work related to infinite dilution activity coefficients

The measurements for the infinite dilution activity coefficients of alkanes, alken-1-es, alkyn-1-es, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, tert-butyl methyl ether, and water in the ionic liquid 1-butyl-3-methylimidazolium thiocyanate [BMIM][SCN] were determined by gas liquid chromatography at the temperatures from 298.15 K to 368.15 K (Domańska and Laskowska, 2009). The ratio for hexane/benzene, cyclohexane/benzene, hexane/thiophene, and other separations problems were computed from γ_{13}^{∞}. The results revealed that IL ([BMIM][SCN]) has the potential to separate organic compounds and can be used in the desulphurization process.

The activity coefficients at infinite dilution, γ_{13}^{∞}, for alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanol, ketones and water in the 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ($[BMIM]^+[Tf_2N]^-$) were measured at temperatures of (323.15, 333.15, 343.15, 353.15 and 363.15) K . The selectivities, $S_{ij,s}^{\infty}$, and capacities, $K_{j,s}^{\infty}$ were determined for the separation of alkane/aromatic, alkane/alk-1-ene, cycloalkane/aromatic and water/alkan-1-ol, using gas-liquid chromatography. The investigated solvent was compared with the previously investigated ionic liquids and industrial solvents.

The infinite dilution activity coefficients of the organic solvents and water in 1-butyl-3-methyl-imidazolium dicynamide [BMIM][DCA] were measured at the temperatures of (318.15-368.15) K, using the GLC. The results revealed that the proposed ILs may be utilized as an optional solvent in separation of alkenes from alkanes. The highest selectivity value of 2.31 was obtained for the separation problem of hexane/hex-1-ene.

Techniques used to predict measurements for infinite dilution activity coefficients

Several techniques were developed to determine the infinite dilution activity coefficient as listed below and are explained in greater details in chapter four:

- Gas-Liquid Chromatography (Letcher, 1980).
- Differential ebulliometry (Gautreaux Jr. and Coates, 1955).
- Headspace chromatography (Hussam and Carr, 1985).
- Dew-point method (Trampe and Eckert, 1993).
- Microdroplet evaporation (Ray and Venkatraman, 1995).
- Inert gas stripping (Lerol et al., 1977).
- Differential Static Cell Method (Alessi et al., 1991).

In this study, the gas liquid chromatography was used as a technique to measure the values of infinite dilution activity coefficients for the solutes in the limonene solvent.

2.7. Gas Liquid Chromatography

This technique involves the spreading out of organic solutes between two phases, solid packing coated with solvent and mobile phase. In the Gas liquid Chromatography two phases can interact with each other. Solid packing provides larger surface area as to allow more contact between stationary and mobile phase. The liquid is held on the surface and in the pores of solid support, whereas the mobile phase flows continuously through the spaces between solid particles (Anderson et al., 1970).

Small quantity of solute is injected into the column at the inlet. The injected solute quickly evaporates by heated injector point, as it carried out in the column by mobile phase, it interacts with solid packing coated with solvent whereby it is adsorbed and de-adsorbed. As it comes out at the far end of the column it is detected by thermal conductivity detector. The speed at which the peak travels through the column is less that of the mobile phase and it depends on the distribution coefficient of solute between two phases (Anderson et al., 1970).

Equilibrium it is set up between liquid phase and the carrier gas phase so that the sample remains in the gas phase when the solute reaches the column. As it moves through the column it equilibrates with the stationary phase at the same time dissolved material in the stationary phase and move to the gas phase as to balance the equilibrium with the carrier gas (Conder and Young, 1979). The retention time for each sample depends on two factors, flow rate of carrier gas and the partition coefficient of the solute between the carrier gas and the liquid phase. The higher the flowrate of carrier gas the less time it takes for the solute to be adsorbed by the solvent.

Following assumptions are made as to determine the infinite dilution activity coefficient of solutes based on theory (Purnell, 1962):

- The column can be divided into a large number of theoretical plates.
- The amount of solute injected into the column occupies small portion of the column.
- For low solute concentration, the partition coefficient it is constant throughout.
- Mass transfer from gas to solvent it is negligible.

CHAPTER 3

THERMODYNAMICS FUNDAMENTALS

Chapter overview

This chapter intends to provide insight into the thermodynamics fundamentals and equations used to compute the infinite dilution activity coefficients. The development of gas-liquid chromatography is detailed with the equations for the activity coefficient, partial excess molar enthalpy, selectivity and capacity.

3.1. Infinite dilution activity coefficient

Definition

Activity coefficients are used to account for the deviation of phase equilibria from ideal behaviour. The activity coefficient of a non-ideal solution is defined as the ratio of the activity a_i, and the mole fraction x_i,

The activity coefficient (γ_i) of each species in a solution is defined by the following equation:

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i} \qquad (3\text{- }1)$$

Whereby: $\hat{f}_i$ is the fugacity of component i in solution

f_i pure component fugacity

x_i mole fraction of i in liquid phase

Departure of activities from mole fractions when solutions are non-ideal based on concentrations in mole fractions are defined following equation:

$$\alpha_i = x_i \gamma_i \qquad (3\text{- }2)$$

3.2. Importance of IDACs

Infinite dilution activity coefficient (IDAC) is defined as the limiting value of activity coefficient of the solute when its concentration approaches zero (Seader et al., 2011). It is used to account for the deviation of real solutions from ideal solutions. The activity coefficient at infinite dilution is especially important because it describes the extreme case in which only solute - solvent interactions contribute to non ideality. The activity coefficient at infinite dilution is a crucial parameter in the prediction of phase partitioning of a solute. It also one of the basic thermodynamic properties used to obtain the adjustable parameters in various activity coefficient models of multi – component systems. In most cases it is used for the characterization behaviour of a single solute molecule completely surrounded by solvent molecules, which represent the maximum non ideality of the solute behaviour in solution. This means that the activity coefficient of a solute provides specific information about the molecular interactions between the solute and the solvent, eliminating solute – solute interactions (Muzenda et al., 2011).

The infinite dilution activity coefficient can guide on selecting the potential solvent for particular separation processes and it can be used to design commercial separation processes. The significant application of the activity coefficient at infinite dilution comprises the description of the behaviour of liquid mixtures in their dilute regions (Nkosi, 2017). Typical uses of infinite dilution activity coefficient are:

- In industrial processes involving the production of high purity products.
- Environmental pollution remediation processes focused on the removal of traces of impurities which is costly and energy-intensive.

The system normally deviates from the ideal behaviour in the infinite dilute concentration range. It is stated that the activity coefficients at infinite dilution are mostly accurate when describing the behaviour of the system in the diluted region (Raal and Mühlbauer, 1998). The uses of these activity coefficients for practical and theoretical are as follows:

- Screening of extractive distillation solvents (Perry and Green, 1998).
- Screening of liquid extraction solvents (Palmer, 1987).
- Screening for potential azeotropes (Palmer, 1987).
- Provide theoretical information about solute-solvent interaction in the absence of solute-solute interactions (Howell et al., 1989).

3.3. Selectivity and capacity

The infinite dilution activity coefficient is interrelated to other parameters namely selectivity and capacity. These parameters play a vital role in the separation of high purity chemicals because the removal of traces of impurities requires the greatest separation effort. The IDAC's values are required to select suitable solvents for separation processes and to identify separation problems such as azeotropes, close-boiling points and miscibility gaps, aiding in the design of various separation units (Seader et al., 2011). The entrainer with the highest selectivity is considered to be the most promising for separation of the mixture and it has been widely accepted criteria for solvent selection (Jiménez Esteller and Costa-López, 2013, Kyle and Leng, 1965) and indicate that the use of the solvent with the highest selectivity will yield the lowest total annual costs for the extractive distillation process (Lei et al., 2003). Equation (3- 3) and (3- 4) are used to calculate the selectivity and capacity at infinite dilution with respect to the *i/j* system.

$$S_{ij,s}^{\infty} = \frac{\gamma_{is}^{\infty}}{\gamma_{js}^{\infty}} \tag{3- 3}$$

And

$$K_{ij,s}^{\infty} = \frac{1}{\gamma_{js}^{\infty}} \tag{3- 4}$$

Where ($S_{ij,s}^{\infty}$) is the selectivity at infinite dilution of solvent (s) for the system consisting of components i and j. $\gamma_i^{\infty}$and γ_{js}^{∞} represent the limiting coefficient of *i* and *j* respectively in the solvent (s). K_{js}^{∞} is the capacity at infinite dilution of solvent (s), which is used to determine the maximum amount of species *j* that can be dissolved in the solvent.

3.4. Temperature dependence of activity coefficient

The temperature dependence of the activity coefficient can be used to calculate the partial molar excess enthalpies at infinite H^Ecan be calculated using Gibbs-Helmholtz Equation (3- 5)

$$\left[\frac{\partial\left(G^E/_{RT}\right)}{\partial T}\right]_{p,x} = -\frac{H^E}{RT^2} \qquad (3\text{-}\ 5)$$

whereas at infinite dilution it gives:

$$\left(\frac{\partial \ln\gamma_i^\infty}{\partial T}\right)_{p,x} = -\frac{H^E}{RT^2} \qquad (3\text{-}\ 6)$$

and

$$\left(\frac{\partial \ln\gamma_i^\infty}{\partial\left(1/_T\right)}\right)_{p,x} = -\frac{H_i^{E,\infty}}{R} \qquad (3\text{-}\ 7)$$

Where and R are the slope of the fitted line partial excess molar enthalpy at infinite dilution that can be obtained directly from the straight line as derived from Equation (3- 7) and ideal gas constant; and (T) is the experimental temperature. Equation (3- 8) was used to determine the standard deviation of measured values from the fitted line.

$$\ln\gamma_i^\infty = A + B/T \qquad (3\text{-}\ 8)$$

3.5. Equations for the calculation of IDAC

Gas Liquid chromatography

The measurements of the retention volumes for the gas liquid chromatography (GLC) could produce important physico-chemical data as suggested by James and Martin (1952). It has been highlighted that the potential of GLC to study and analyses the interaction of volatile solutes with non-solvent by measuring the infinite dilution activity coefficient using GLC (Hoare and Purnell, 1956). In the GLC the solid support in the packed column, it is coated with the non-volatile solvent and the gas phase flows through in between the spaces, thus increasing the interaction with solutes and non-volatile solvent in the stationary phase. Helium gas it is used as the carrier gas to transport the solute throughout the column at the constant flow rate.

Small amount of solute is injected into the inlet of the column, the formed solute zone or peak moves through the column by the carrier gas and emerges at the end of the column as observed by thermal conductivity detector in a form of a peak

The infinite dilution activity coefficient is calculated by using the thermodynamics of the experimental data. The partition distribution coefficient, K_L of the solute between two phases was defined by Conder and Young (1979) as follows:

$$K_L = \frac{q}{c} = \frac{C_L}{C_M} \tag{3- 9}$$

whereby,

$$C_L = \frac{y_1 n_3}{V_L} \tag{3- 10}$$

and,

$$C_M = \frac{y_1 n_2}{V_G} \tag{3- 11}$$

Where c (and C_M) is the concentration of solute in the mobile phase and q (and C_L) is the concentration of solute in the liquid phase when the solute as a vapor phase and liquid equilibrium. When the solute is in equilibrium, the chemical potential in both the liquid and mobile phase it is assumed to be equal:

$$\mu_i^L = \mu_i^M \tag{3- 12}$$

and,

$$\mu_i = \mu_i^o + RT\ln\alpha_i \tag{3- 13}$$

Substituting activity ($\propto_i$) by concentration and substituting into Equation (3- 12) and (3- 13):

$$\mu_i^{0.L} + RT\ln C_L = \mu_i^{o,M} + RT\ln C_M \tag{3- 14}$$

and,

$$K_L = \frac{C_L}{C_M} = \exp\left(\frac{\Delta\mu_i^0}{RT}\right) \tag{3- 15}$$

The partition coefficient *K*L and $\Delta\mu_i^o$ ideally are constants. The net retention volume, V_N is directly proportional to the partition coefficient K_L and the volume of the liquid phase, V_L as follows:

$$V_L = K_L V_L \tag{3- 16}$$

Whereby K_L can be used to determine the mean column pressure (Lobien and Prausnitz, 1982)

Expressing Equation (3- 16) in terms of mole fractions and number of moles as follows:

$$K_L = \frac{x_i n_3 V_G}{y_1 n_2 V_L} \tag{3- 17}$$

x_i and y_1 are mole fractions of solutes in the liquid phase and gas phase respectively. n_3 is the number of moles of solvent in the liquid phase and n_2 is the number of moles of carrier gas component in the mobile phase. V_G and V_L are the volumes of the gas phase and liquid respectively.

Considering that the vapor phase (V_G) is ideal gas and its volume is given as follows:

$$V_G = \frac{n_2 RT}{P} \tag{3- 18}$$

Whereas the activity coefficient at any concentration is defined as:

$$P_i = \gamma_i x_i P_i^o \tag{3- 19}$$

P_1 is the partial vapor pressure and P_i^o is the saturated vapour pressure. The partial pressure of solute p_1 is expressed in terms of the total pressure *P* as follows:

$$P_i = yP \tag{3- 20}$$

And substituting Equation (3- 19) and (3- 20) into (3- 17)

$$K_L = \frac{Pn_3V_G}{\gamma_{13}^o P_i^o n_2 V_1} \tag{3- 21}$$

Expressing Equation (3- 21) using ideal law ($PV=n_2RT$) as suggested by (Porter et al., 1956) as follows:

$$\gamma_{13}^o = \frac{n_3\,RT}{P_i^o K_L V_1} \tag{3- 22}$$

Substituting Equation (3- 19) into (3- 22) and assuming $V_1=V_L$:

$$\gamma_{13}^\infty = \frac{n_3\,RT}{V_N P_i^o} \tag{3- 23}$$

The calculation of the infinite dilution activity coefficient from retention volume, V_N, is possible only if the rough estimated value of γ_{13}^∞ is enough. Compressibility and imperfection of the gas phase must be accounted for greater accuracy. It is assumed that the solute reaches equilibrium between the mobile and stationary phases and that the mobile phase is insoluble in the stationary phase.

Thus, the infinite dilution activity coefficient of solutes was calculated according to the equations developed by (Everett, 1965) and (Cruickshank et al., 1969) Equation (3- 23) through the solute retention (Heintz and Verevkin, 2005):

$$\ln\gamma_{13}^\infty = \left(\frac{n_3\,RT}{V_N P_i^o}\right) - \frac{(B_{11} - v_1^*)P_i^o}{RT} + \frac{(2B_{12} - v_1^\infty)J_2^3 P_o}{RT} \tag{3- 24}$$

Equation (3- 24), γ_{13}^{∞} is the activity coefficient of solute i at infinite dilution in the stationary phase, n_3 is the number of moles of solvent, R is the universal gas constant, T, is the column temperature, P_i^* is the saturated vapor pressure of solute i, V_N represents the net retention volume of solute obtain in Equation (3- 25) (Letcher, 1978):

$$V_N = (J_2^3)^{-1} U_o (t_r - t_G) \frac{T_{col}}{T_f} \left[1 - \frac{P_w^o}{P_o}\right] \tag{3- 25}$$

Where t_r represents the retention time, $t_G$the dead time, $U_o$the flow rate of helium gas, T_{col} column temperature, T_f flowmeter temperature, P_w^o the saturation vapor pressure of water at T_f and P_o represents the pressure at the column outlet. In Equation (3- 24), the second and third serves as a correctional term from the nonideality of the mobile gas phase and the effect of pressure. B_{i1} is the second virial coefficient of the solute, B_{i2} is the mixed second virial coefficient of the solute (i) with a carrier gas (2), v_i is the liquid molar volume of pure solute and v_i^{∞} is the partial molar volume of the solute in the stationary phase (3) at infinite dilution. P_i^* values were calculated from the Antoine equation with coefficients (Poling et al., 2000).

Molar volumes of solutes v_1^* were estimated using the experimental densities, partial molar volumes of solutes at infinite dilution v_1^{∞} assumed to be equals to v_i. Equation (3- 26) was used to calculate B_{i1} and B_{i2} (McGlashan and Potter, 1962). The mixed critical constant P_c, $T_c B_{i1}, V_c, I_c$ and acentric factor ω were needed for calculation (Poling et al., 2000).

$$B/V_c = 0.43 - 0.886\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375\,(n-1)\left(\frac{T_c}{T}\right)^{4.5} \tag{3- 26}$$

Where n represents the number of carbon atoms in the solute molecule. Mixing rules were used to determine the values of mixed properties for critical properties (T_c, V_c and Ionisation energy) of pure components (Hudson and McCoubrey, 1960).

$$T_C = 128\,(T_{C11}.T_{C22})^{1/2}\,(I_{C11}.I_{C22})^{1/2}\left(V_{C11}.V_{C22}/I_{C12}\right) \tag{3- 27}$$

whereby,

$$I_{C12} = (I_{C11} + I_{C22})^{1/2} \left(V_{C11}^{1/3} + V_{C12}^{1/3}\right)^6 \tag{3- 28}$$

and,

$$V_{C12} = \frac{1}{8} \left(V_{C11}^{1/3} + V_{C12}^{1/3}\right)^3 \tag{3- 29}$$

whereas,

$$n_{12} = \frac{n_1 + n_2}{2} \tag{3- 30}$$

The pressure correction term is given by Everett (1965):

$$J_2^3 = \left(\frac{2}{3}\right)\left[\frac{\left(\frac{P_i}{P_o}\right)^3 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1}\right] \tag{3- 31}$$

Where P_i and P_o represents the pressure at the column inlet and outlet of the GC.

The gas-liquid partition coefficients for the solute partitioning between helium gas carrier and limonene solvent was determined from the retention of the solutes using the following equation:

$$\ln(K_L) = \ln\left(\frac{\rho_3 V_N}{m_3}\right) - \frac{(B_{i2} - v_1^{\infty})J_2^3 P_o}{RT} \tag{3- 32}$$

Whereby ρ is the density of limonene at temperature T and m_3 is the mass of limonene.

CHAPTER 4

REVIEW OF EXPERIMENTAL TECHNIQUES AND EQUIPMENT

Chapter overview

This chapter focuses on the few relevant experimental techniques and equipment used on the determination of the infinite dilution activity coefficients. It outlines the advantages and disadvantages of each technique. The following techniques are commonly used for the determining the measurements for the infinite dilution activity coefficients data:

- Gas-Liquid Chromatography (Letcher, 1980).
- Differential ebulliometry (Gautreaux Jr. and Coates, 1955).
- Headspace chromatography (Hussam and Carr, 1985).
- Dew-point method (Trampe and Eckert, 1993).
- Inert gas stripping (Lerol et al., 1977).
- Dilutor cell (Lerol et al., 1977).
- Dilutor cell (Richon et al., 1985).
- Differential Static Cell Method (Alessi et al., 1991).

4.1. Gas Liquid chromatography

The measurements of the retention volumes for the gas liquid chromatography (GLC) could produce important physical-chemical data (James and Martin, 1952). It has been highlighted that the potential of GLC to study and analyses the interaction of volatile solutes with non-solvent by measuring the infinite dilution activity coefficient using GLC (Hoare and Purnell, 1956). In the GLC the solid support in the packed column, it is coated with the non-volatile solvent and the gas phase flows through in between the spaces, thus increasing the interaction with solutes and non-volatile in the stationary phase. Helium gas it is used as the carrier gas to transport the solute throughout the column at the constant flow rate.

Small amount of solute is injected into the inlet of the column, the formed solute zone or peak moves through the column by the carrier gas and emerges at the end of the column as observed by thermal conductivity detector in a form of a peak. The infinite dilution activity coefficient it is calculated by using the thermodynamics of the experimental data.

In the system whereby solvent has moderate volatility with less accuracy, the GLC can be used (Thomas et al., 1982). Simplified schematic diagram of the equipment is presented in Figure 4- 1 (de Castro Vasconcellos et al., 2015). Table 4- 1 presents advantages and disadvantages of the GLC (Weir and De Loos, 2005).

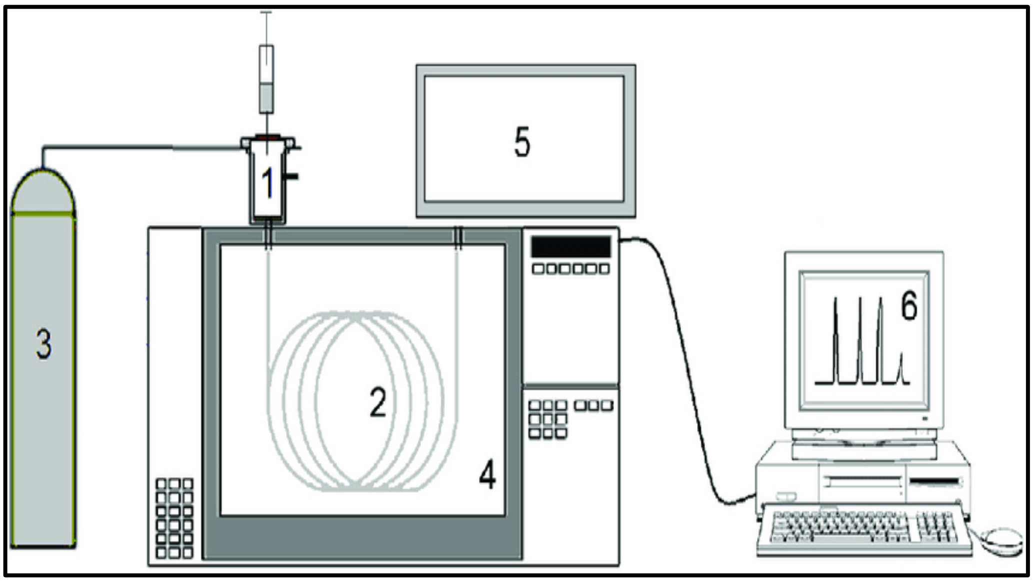


Figure 4- 1: Schematic diagram for gas liquid chromatography (de Castro Vasconcellos et al., 2015).

1 – Sample injector point; 2- Packed column (oven); 3- Helium (carrier gas); 4- Oven; 5- Thermal conductivity detector (TCD); 6- Retention time analysis (Chart recorder)

Table 4- 1: Advantages and disadvantages of gas liquid chromatography (Weir and De Loos, 2005)

Advantages	Disadvantages
Gas chromatography experiment is relatively fast. Different solutes can be studied at once.	Method suited for low volatility solvents.
It can separate and purify components of mixed sample.	Activity coefficient for Solvent in solute cannot be measured.
Only small quantities of solutes and solvent are required.	It is limited to specific experimental temperature ranges.
Easy to operate it at any temperature within the capacity of the equipment.	

4.2. Differential ebulliometry

This technique presents the correlations for the activity coefficient ratio given the following data (Gautreaux Jr. and Coates, 1955).

- Isobaric (T-x_i) data
- Isobaric (T-y_i) data
- Isothermal (P-x_i) data
- Isothermal (P-y_i) data

This technique can be used to measure isobaric T-x_i and isothermal P-x_i data. Ebullionmeters are connected to the pressure manifold as a set requirement for the differential ebulliomerty and as result each pressure is the same in the ebulliometer. The boiling point difference between the pure solvent and dilute mixtures are measured. It is important in the method that the liquid concentration be accurately known as suggested by (Raal and Mühlbauer, 1998) and (Raal, 2000). The procedure may be repeated with the diluted mixtures of the solvent in solute, in this way infinite dilution activity coefficient may be determined. This technique is suitable for systems with low relative volatility; however, it is problematic for system involving of various non-volatile components.

This method fails for soluble solutes as a result large quantity of solvent are required and the temperature measuring devices available are not sensitive enough to detect the boiling point temperature elevation by the introduction of solute into the solvent (Lobien and Prausnitz, 1982). Schematic diagram of the equipment is presented in Figure 4- 2 (Richon, 2011) and with the advantages and disadvantage in

Table 4- **2** (Harris, 2000).

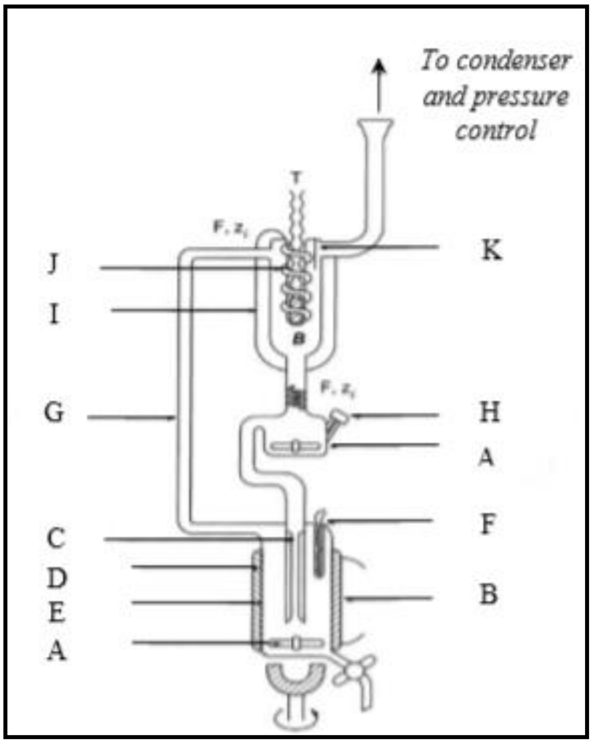


Figure 4- 2: Differential ebulliometer schematic diagram (Richon, 2011).

A – Magnetic Stirring bar; B – Heating coil; C – Capillary; D – Reboiler; E – Fused ground glass; F – Temperature sensor (Pt 100); G – Cottrell pump; H – Sample septum (mixing spiral); I – vacuum jacket; J – Fussed glass spiral; K – Splash guard

Table 4- 2: Advantages and disadvantages of differential ebulliometry (Harris, 2000).

Advantages	**Disadvantages**
It is used for systems with high relative volatility or where volatilities of two components are the same. It is a time-consuming method. It requires lot of expertise.	It owes it popularity to the fact that other methods are not applicable to systems where solutes and solvent have similar volatilities.

4.3. Headspace chromatography

This technique of headspace in GC shows the gas phase in the chromatography vial above the sample. It is defined as the vapor above a liquid or solid phase of a sample. It is the analysis of vapor lying in equilibrium over liquid or solid sample in sealed vial. The sample is heated on an oven at a controlled temperature until the vapor phase reaches equilibrium with the sample phase. With is technique only volatile components are analysed, nonvolatile components remain in the sample vail and it is referred as the cleanest form of GC analysis since most of nonvolatile remain in the sample vail (Sithersingh, 2018). Headspace method as presented in Figure 4- 3 (Kolb and Ettre, 2006) does not make pressure measurements, which confirms the thermodynamic consistency by the area test (Redlich and Kister, 1948).

This technique can be performed in different ways as listed below (Sithersingh, 2018):

- Static headspace extraction (SHE)
- Dynamic headspace extraction (MHE)
- Multiple headspace extraction (MHE)
- Solid phase micro extraction (SPME)

When the introduction of flame and argon ionization detectors in late 1950s, the use of headspace GC was accelerated due to its ability to investigate volatile organic compounds. These detectors were more sensitive that thermal conductivity detector and small quantities of odorous compound were detected (McWilliam, 1983).With these detectors could detect small quantities of volatile compounds and they were used to investigate range of peppermint oil, pear, banana and coffee samples (Weurman, 1961). The advantages and disadvantages are listed in Table 4- 3 (Sarafraz-Yazdi and Amiri, 2010).

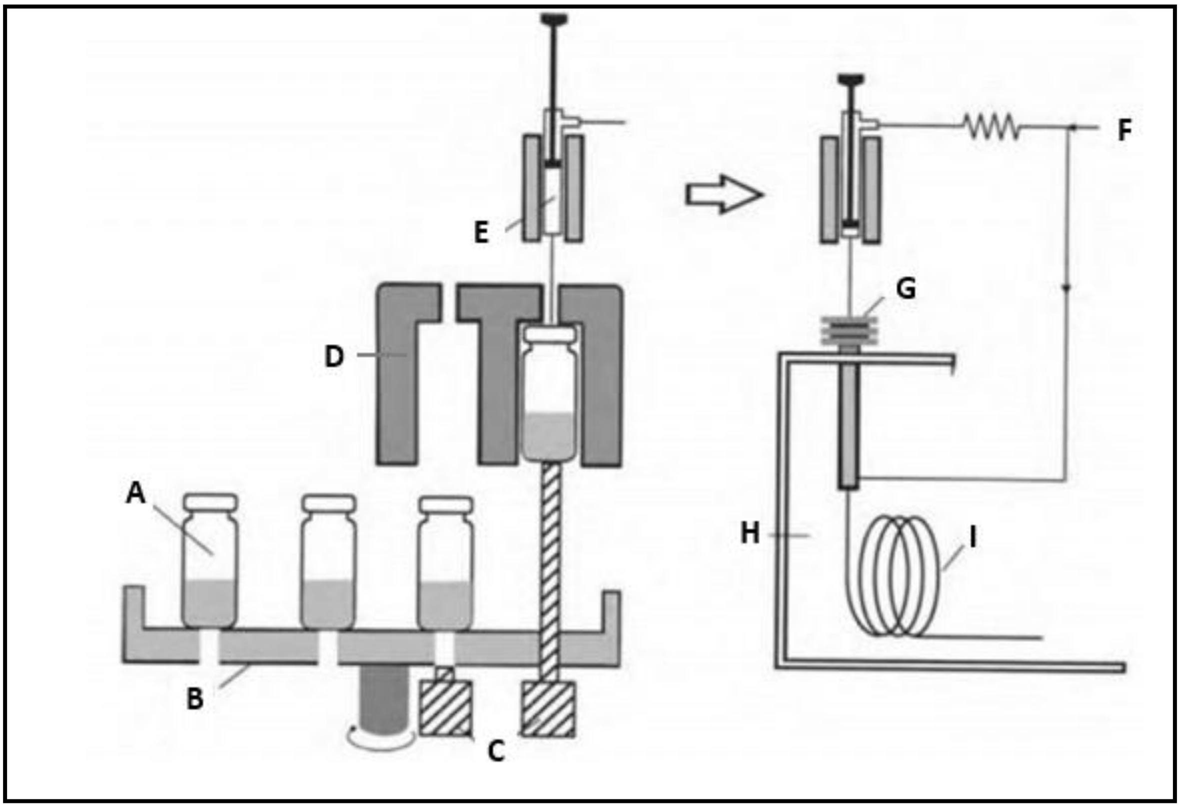


Figure 4- 3: Automated schematic diagram of headspace chromatography (Kolb and Ettre, 2006).

A – Vial; B – Carousel; C – cylinder; D – Heaster; E – Syringe; F – Carrier gas; G – Injector; H – Chromatography; I – Column

Table 4- 3: Advantages and disadvantages of headspace chromatography (Sarafraz-Yazdi and Amiri, 2010).

Advantages	Disadvantages
It is easy to use and cost effective. Excellent cleaning of samples with complex composition. It can extract volatile and water-soluble analytes. It is not a time-consuming method.	Low sensitivity and accuracy.

4.4. Dew-point method

Dew point method was developed as to determine the infinite dilution activity coefficient of dilute vapor phase (Trampe and Eckert, 1993). It is applicable to systems with low solute volatility, whereby other methods like headspace chromatography or ebulliometer are less precise. The method it is slightly the same as differential ebulliometer as it involves the change of temperature of the dew point of vapor solvent when dilute amount of solute is added.

This technique revolves around a general eastern model D2 chilled mirror as shown in Figure 4- 4 and Figure 4- 5, whereby it is used for primarily for measuring humidity of vapor samples (Trampe and Eckert, 1993). The advantages and disadvantages are listed in Table 4- 4 (Trampe and Eckert, 1993, Fowlis and Scott, 1963).

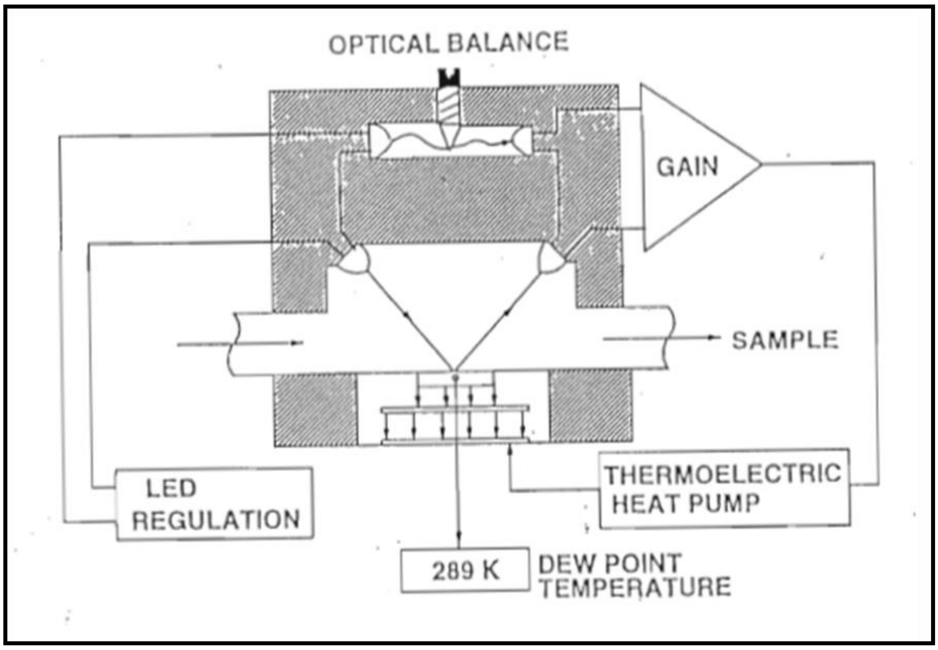


Figure 4- 4: Dew point sensor (Trampe and Eckert, 1993).

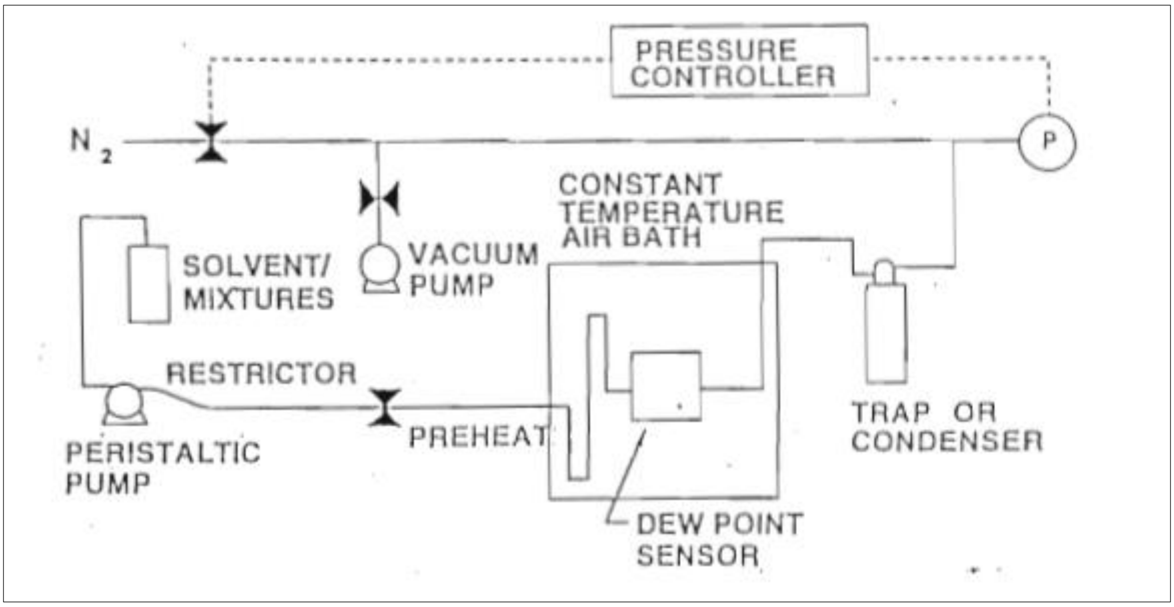


Figure 4- 5: Experimental set up for measuring infinite dilution activity coefficient (Trampe and Eckert, 1993).

Table 4- 4: Advantages and disadvantages of Dew-point (Trampe and Eckert, 1993).

Advantages	Disadvantages
Applicable to systems of low volatility.	Solvents with high purity are required.

4.5. Inert gas stripping

The inert gas stripping technique which is referred as dilutor method and as well as continuous gas extraction technique (Dobryakov and Vitenberg, 2006, Vitenberg, 2003). This method was developed by (Fowlis and Scott, 1963) whereby it was used to calibrate the detector for the chromatography. The equilibrium cell design was modified as to account for mixing by (Ritter and Adams, 1976) and (Burnett, 1963) used dilutor method to determine the partition coefficients for vapor-liquid equilibrium and it was later developed by (Lerol et al., 1977) to determine the infinite dilution activity coefficient. After Leroi, lot of work has been done as to improve the inert gas stripping method, such as the modification of the apparatus as to observe viscous and foaming mixtures by (Richon et al., 1985). Analysis for both vapor and liquid mixture were combined as to determine the measurements for wide range of concentration

(Hradetzky et al., 1990, Ovečková et al., 1991, Wobst et al., 1992). The cell for high pressure measurements was developed by (Legret et al., 1983) and systems consisting of multiple solutes (Bao and Han, 1995).

Inert gas stripping method the flow of gas passes through liquid mixture and strips the more volatile solute from the diluted mixture containing solvent. The gas containing traces amount of solute it is analysed using gas chromatography as to determine the retention time using peak profile and the infinite dilution activity coefficient is calculated. This technique applies to non-volatile or volatile solvent which may be less volatile than the solute. The illustration of the equipment set up for the inert gas stripping method as shown in Figure 4- 6 and with the advantages and disadvantages presented in Table 4- 5 (Tumba, 2010).

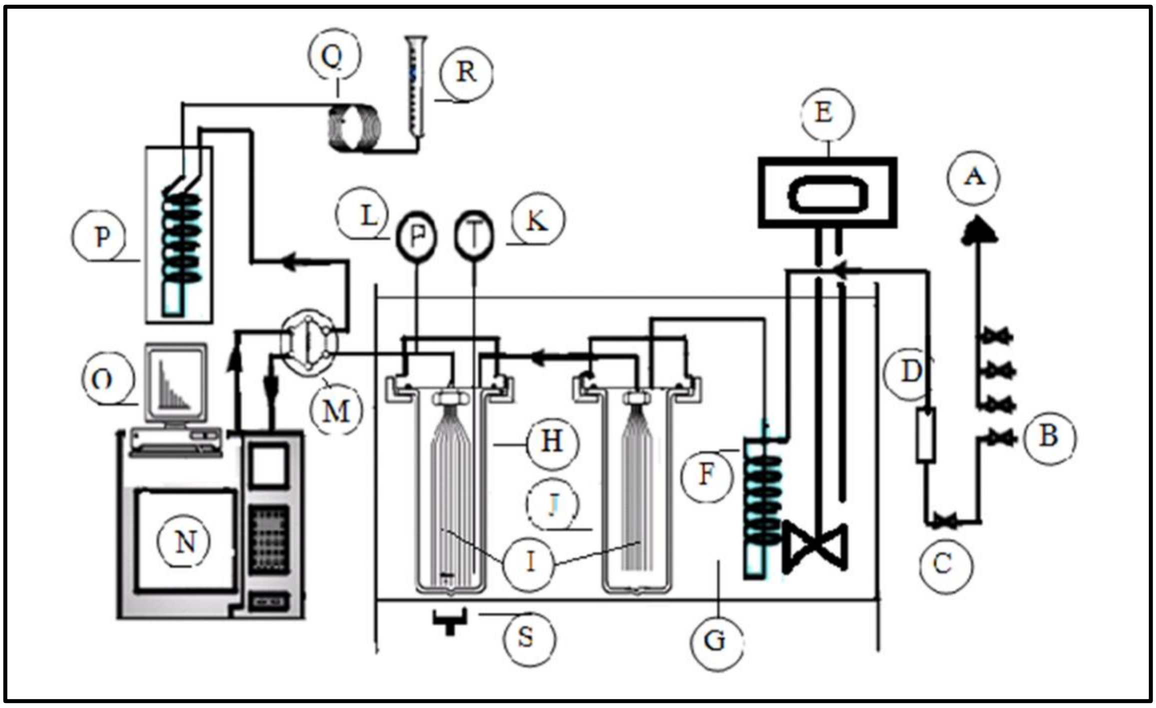


Figure 4- 6: Schematic diagram for the inert gas stripping method (Tumba, 2010).

A- Helium, Nitrogen and air supply for the GC; B- Nitrogen line; C- Valve; D- Flow regulator; E- Immersion temperature controller; F- Coil tube (Heat exchanger); G- Transparent acrylic bath; H- Dilutor cell; I- Capillaries; J- Pre-saturation cell; K- Platinum resistance thermometer; L- Pressure transducer; M- Sampling valve; N- GC apparatus; O- PC monitor; P- Cold trap; Q- Coil tube (Heat exchanger); R- Soap bubble flow-meter; S- Magnetic stirrer.

Table 4- 5: Advantages and disadvantages of inert gas stripping method Tumba (2010).

Advantages	Disadvantages
GC calibration not required; only peak area ratios are used in calculations.	Purification of solute is required.
Systems with high volatility solvents can be measured.	Systems with low volatility solutes are difficult to measure.
Mixture of different solvent can be investigated.	Good contact between gas and liquid is needed as to yield better results.
Mixture of solutes can be studied at once**.**	

Major improvements on the inert gas stripping method

Over the past years various ways have been obtained as to improve the inert gas stripping method since its establishment by Leroi *et al*. (1977). These improvements are as follows:

- Establishment of inert gas stripping method by Leroi *et al*. (1977).
- Introduction of correctional factor (Duhem and Vidal, 1978).
- Modification of dilutor cell by Richon *et al*. (1985).
- Use of double cell technique for highly volatile solvent systems (Dolezal et al., 1981) and (Doležal and Holub, 1985).
- Use of advanced cell for investigating viscous or foaming mixtures by Richon *et al*. (1985).

4.6. Dilutor cell designed

Leroi *et al*. (1977) designed a basic dilutor cell as to measure the infinite dilution activity coefficient. The fritted glass disk which is used to disperse the carrier gas in fine bubbles through solvent as shown in Figure 4- 7. The dilutor cell holds approximately 25 cm^3 of solvent and the small amount of solute was introduced into the cell by the means of syringe through septum.

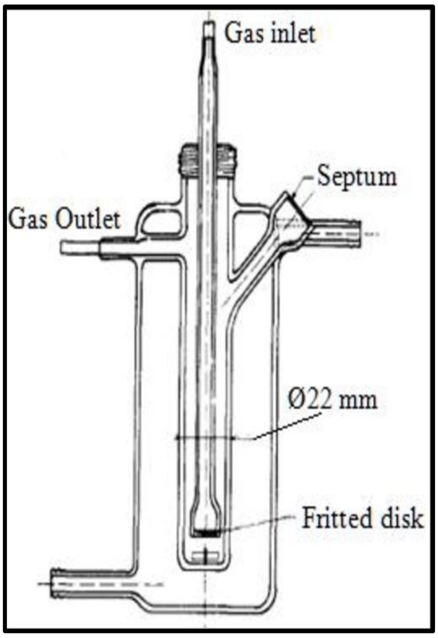


Figure 4- 7: Dilutor cell (Lerol et al., 1977).

Richon *et al*. (1985) modified the dilutor cell which was previously designed by Leroi *et al*. (1977). Richon *et al*. (1985) used the capillaries instead of fritted glass disk, this was to allow bubble size to be uniform across the dilutor cell as shown in Figure 4- 8. This improvement was to increase the mass transfer between the solute and the solvent.

Different dilutor cells were developed over the years as to better the mass transfer between solute and solvent. More of these dilutor cells are explained into greater details by Tumba (2010).

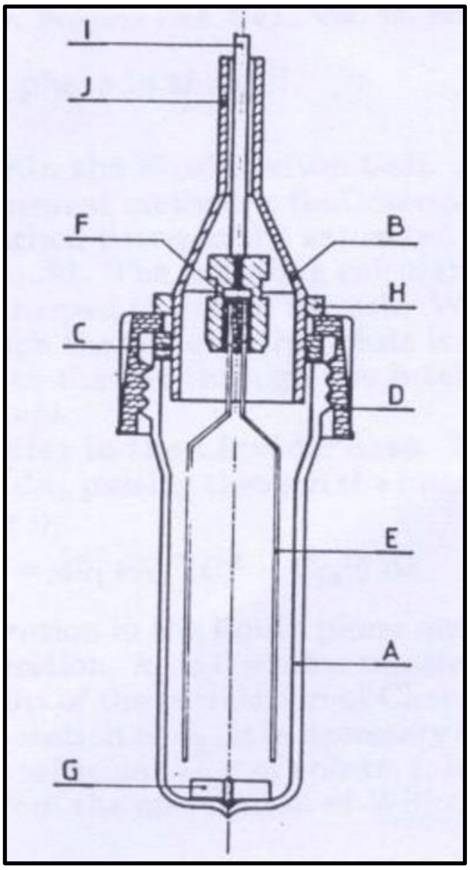


Figure 4- 8: Dilutor cell (Richon et al., 1985).

A – glass still body, B – conical collector of gas outlet, C – gasket, D – plug, E – capillaries, F – Teflon seal, G – magnetic stirrer, H – metallic ring used to adjust the depth of the conical collector B in the still, I – tube for carrier gas inlet, J – gas outlet.

4.7. Differential static cell method

Static cell method it is used to measure the equilibrium vapor pressure of the mixtures of known composition. It is designed in such a way that it measures the equilibrium total pressure of dilute binary mixture at constant bath temperature. It consists of two cells, one cell normally called reference cell, which contains pure solvent and second cell containing mixture of solvent and solute mixture, and pressure differences can be measured directly as to reduce errors in measuring pressure differences. The difficulty about the method is that it requires total evacuation of the cell before introducing liquid mixture as to ensure accurate pressure measurements (Abbott, 1986). Degassing can be done through vacuum sublimation (Maher and Smith, 1979) or distillation (Gibbs and Van Ness, 1972). Figure 4- 9 shows the illustration of static cell apparatus (Alessi et al., 1986). Table 4- 6 presents the advantages and disadvantages of the static cell method (Moollan, 1991).

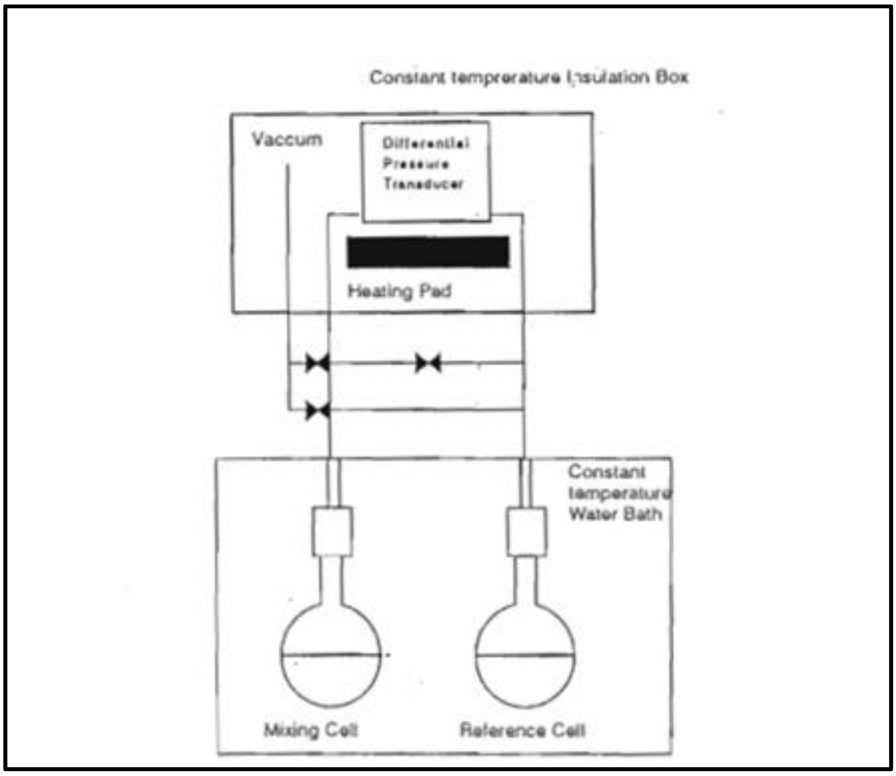


Figure 4- 9: Schematic diagram of differential static cell method (Alessi et al., 1986).

Table 4- 6: Advantages and disadvantages of differential static cell method (Moollan, 1991).

Advantages	Disadvantages
Systems with high volatilities or partial miscible can be measured. Systems with low boiling points solvents can be measured. Pressures are measured directly as to reduce errors.	Solvents must be highly purified and totally free from impurities.

CHAPTER 5

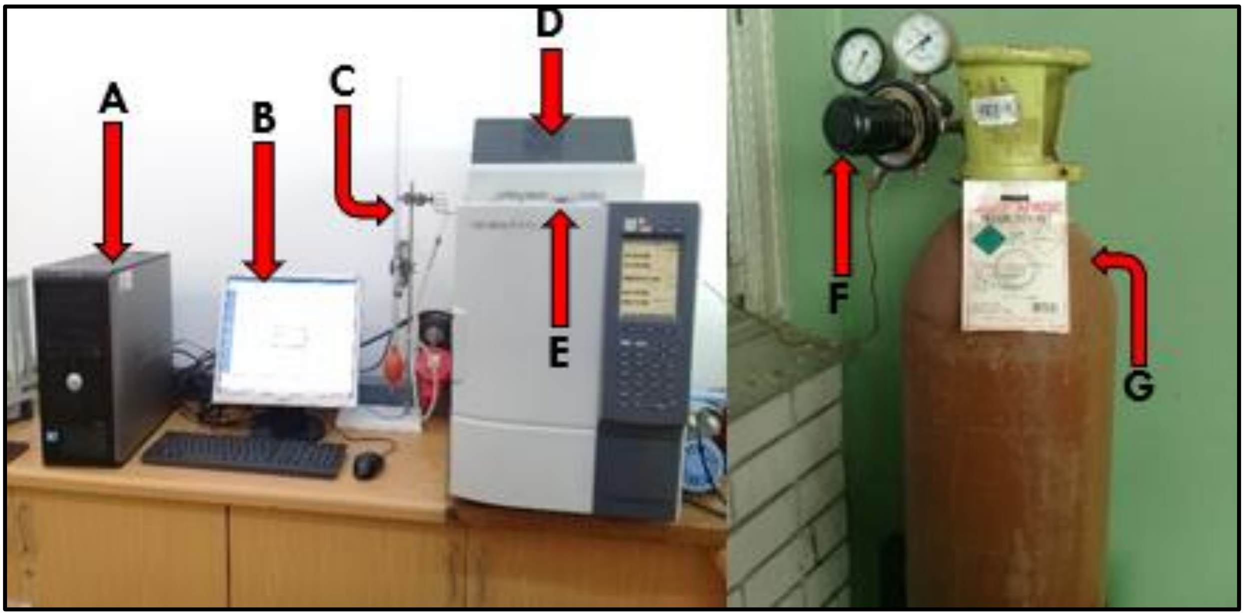
EXPERIMENTAL APPARATUS AND PROCEDURE

Chapter overview

The technique used in this study, the experimental set-up and procedure are explained in this chapter. Detailing the preparation of the column prior to the measurements by the gas liquid chromatography. The uncertainties on the experimental parameters were taken into account and were reported in this chapter.

5.1. Experimental set-up

The gas liquid chromatography (GLC) experimental setup as shown below in Photograph 5-1, using Shimadzu GC-2014. The GLC consist of thermal conductivity detect which is situated at the exit side of the column and its function it is to detect vapourised volatile organic gases leaving the column. During each run, the results of vapourised organic gases leaving the column are displayed on the computer in the form of graphs to determine the retention times of each solute using computerized GC software.



Photograph 5- 1: Experimental set-up for Gas-Liquid Chromatography.

A- Personal computer (pc); B- Display on GC solution software on the computer; C- Bubble flow meter; D- Gas chromatography; E- Sample injection point; F- Gas flow regulator valve; G- Helium (carrier gas)

5.2. Experimental procedure

Prior to the experiments, three stainless steel columns were prepared, one for the test system and two for experimental study. These three identical columns made with 4.1 mm diameter and 500 mm long stainless steel pipe and fittings were bought from Swagelok. Two columns were prepared with two different solvent loadings filled as to see the effect of adsorption during the experiment. Each column was carefully rinsed with soapy water, rinsed with cold water and flushed with acetone as to reduce drying time. When dried, each column was weighed before and after packing, and installed into the oven for conditioning. The column was conditioned for minimum of not less than 2 hours at a temperature of 353.15 K, this was to stabilized the pressure, temperature of the column and to remove any excess impurities present in the column. The mass of the column was recorded using the Sartorius analytical balance BSA224S-CW. Experimental measurements were done at different temperatures between 303.15 K to 333.15 K at the intervals of (303.15, 313.15, 323.15 and 333.15) K, the injector and detector temperatures were set at 523.15 K as to allow solutes to evaporate easily. All solutes were injected in small quantities (0.2- 0.3 µl) due to high sensitivity of a GC, one solute was injected per time per run and the retention time was recorded for calculating IDAC using Equation (3-24). Bubble flow meter was installed at exit side of the gas flow, and it was used to determine the flow rate of the carrier gas which is helium.

Outlet Pressure, P_o

The outlet pressure it was assumed to be equal to the atmospheric pressure since the column is open to the atmosphere. LCD digital air pressure meter SCT-108.001.37 was used to determine the pressure of the surroundings during experimental runs. A photograph of the LCD digital air pressure meter SCT-108.001.37 is given in Photograph 5- 2 and with the list of specifications in Table 5- 1.

Table 5- 1: Specifications of LCD digital air pressure meter SCT-108.001.37.

Air pressure	Type absolute pressure range: 300 ~ 1100mb (HPA); 8.85 INHG ~ 32.45 INHG
	Resolution: 1 MB/HPA; 0.01 INHG
	Sensing time: 15 minutes
Altitude	Altitude range: -700m~+9000m, -2296ft ~+29520ft
	Resolution: 0.1m for -500.0m to 999.9m; otherwise 1m
	Sensing time: 2 seconds
Temperature	Temperature range: -10°C ~ +60°C or +14°F ~ +140°F
	Resolution: 0.1°C OR 0.1°F
	Sensing time: 1 minute
Power	2 x 3 volts
Ambient temperature for plastic case	0°C ~ +50°C OR +14°F ~+122°F

Photograph 5- 2: LCD digital air pressure meter SCT-108.001.37.

Inlet Pressure, P_i

Inlet pressure depended on the gas flow rate set by the GC operator, the pressure drop was recorded for each run and the inlet pressure was calculated as follows:

$$P_i = P_o + \Delta P \tag{5- 1}$$

Temperature control

The control of the column temperature is essential in terms of determining the infinite dilution activity coefficient of each solute. When set on the GC solution software on the computer, the system will automatically adjust the column temperature to the required setpoint, once it has stabilized the system will give a green light for the run to start. LCD digital air pressure meter was used to determine the temperature of the surroundings during experimental runs. A photograph of the LCD digital air pressure meter is given in Photograph 5- 2 and with the list of specifications in Table 5- 1.

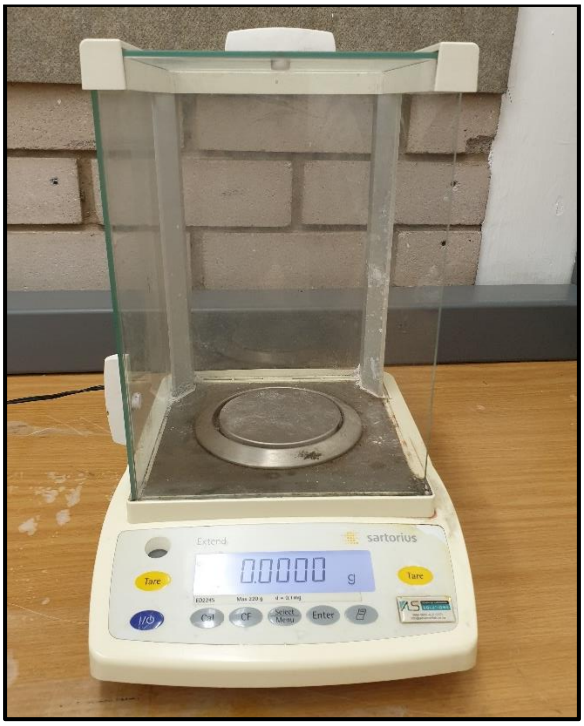
Flow rate of helium gas

The flow rate of carrier gas exiting the column was determined by simply using a soap bubble meter which was inserted at the end of the column. The bottom of the bubble meter consisted of a rubber bung, it is used to form a thin film of bubble and to give it little pressure as it raises up 50 ml burette with a push of gas flow. A stopwatch was used to record the time taken for the bubble to move throughout the burette.

Determination of number of solvents, n_3

Column cleaning and preparations

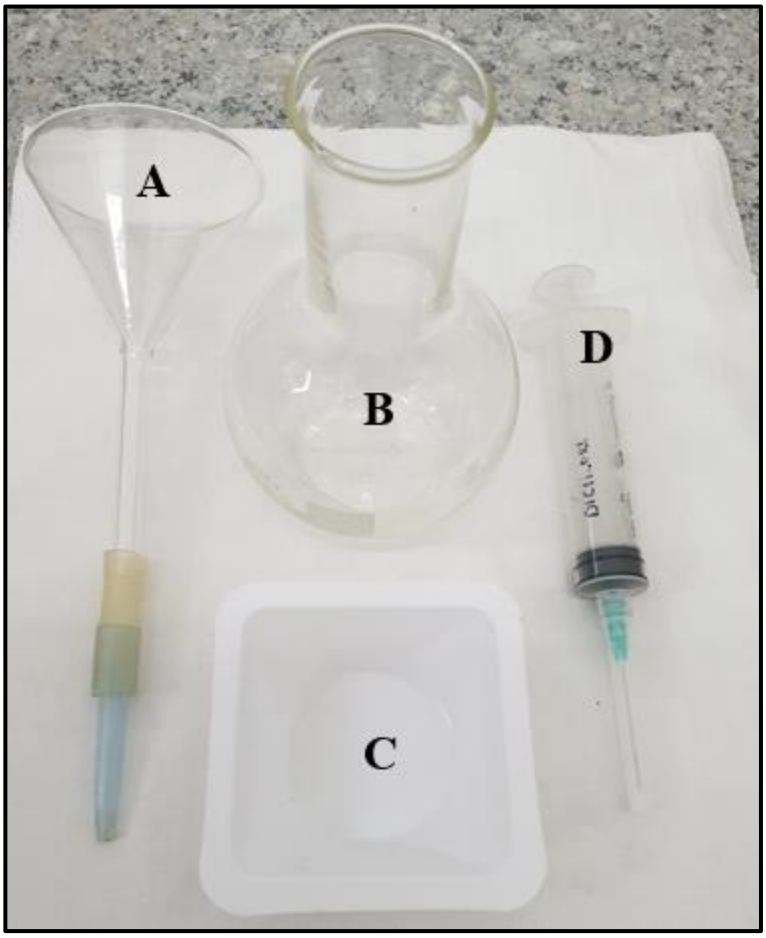
- Stainless steel with a length of 0.5 m and diameter of 4.1 mm was used as a column in the GC. Glassware used for packing the column was washed with soapy water, rinsed with water and flushed with acetone and placed in the oven for drying. Two nuts with ferrous were tightened at each end of the column and weighed using Sartorius analytical balance BSA224S-CW as shown in Photograph 5- 3, with the precision of ±0.00001 g.
- The cleaned empty round bottom flask was weighed and the chromosorb W-HP 80/100 mesh which act as solid support was added to the round bottom flask and weighed.
- The calculated amount of liquid solvent based on percentage loading between 27-35% was added on the solid support and weighed. Refer to Appendix B for a detailed calculation.



Photograph 5- 3: Sartorius analytical balance BSA224S-CW.

Coating solid support with solvent

- Dichloromethane liquid was added using the syringe into the round bottom flask which contained chromosorb and solvent as presented in Photograph 5- 4. This was to allow the solvent to be evenly distributed across the solid support and the total mass was weighed. Refer to Appendix B for a detailed calculation.
- The hollow rubber stopper with a small pipe was inserted at the top of the round bottom flask for the extraction of dichloromethane.

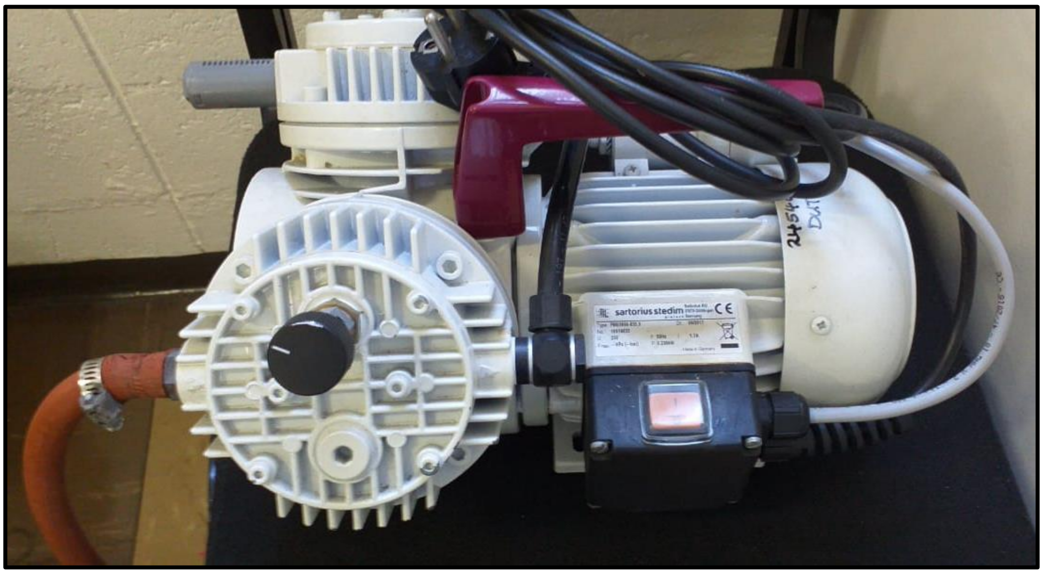


Photograph 5- 4: Laboratory glassware, weir and syringe.

A- Glass funnel; B- Round bottom flask; C- Plastic weir; D- Syringe for adding dichloromethane and limonene

Removal of dichloromethane

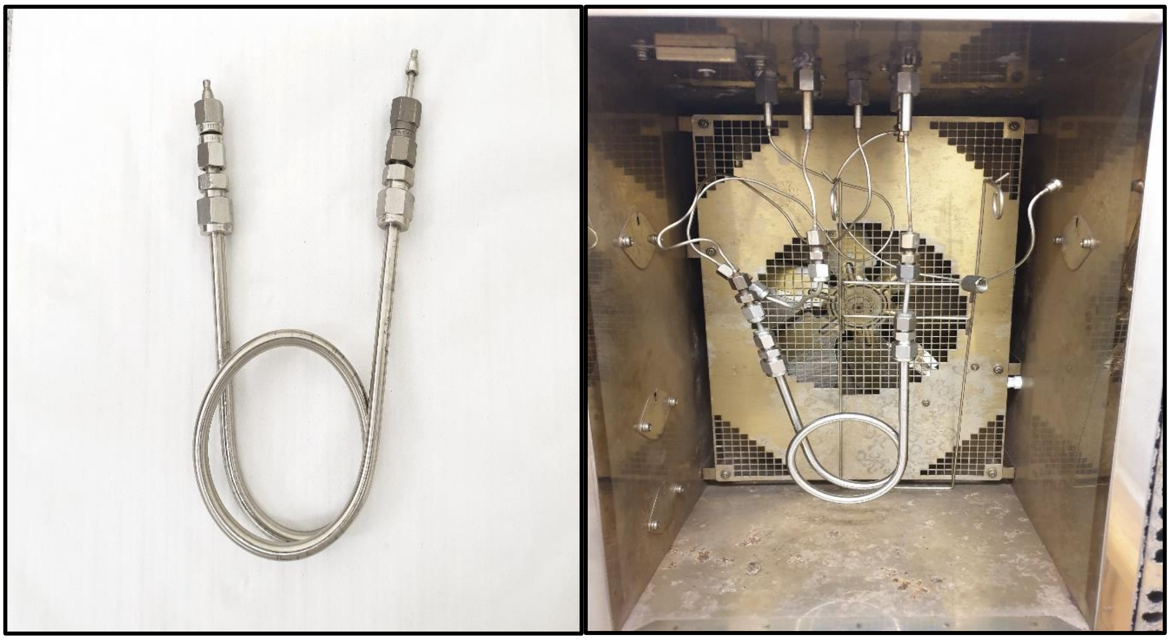
- Sartorius vacuum pump was used to remove dichloromethane by creating a vacuum on the round bottom flask as given in Photograph 5- 5.
- Traces of dichloromethane were removed by placing round bottom flask inside the incubator or oven until all dichloromethane was removed and coated solid support was completely dried. The flask was weighed and compared to the original mass before adding dichloromethane. See Appendix B for a detailed calculation.



Photograph 5- 5: Sartorius vacuum pump.

Packing the column

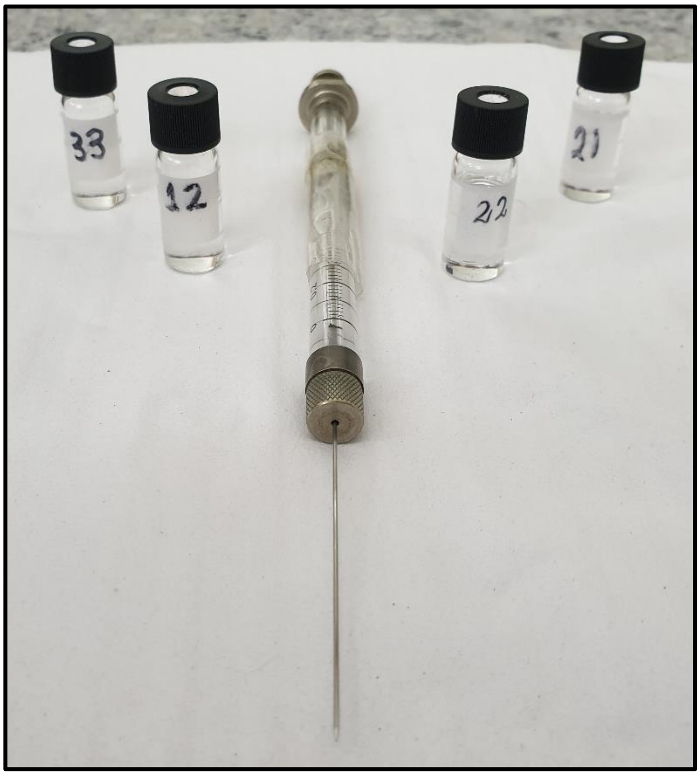
- Glass wool which acts as a stopper was plugged at the one end of the straight column and it was clamped in the rotating stand. The dried coated solid support was added using a glass funnel. The column was tapped lightly to allow coated solid support to fill the column and to ensure that no gaps are left inside the column when packing.
- When the coated solid support not moving anymore in the funnel and it was assumed that the column was completely filled with solid support. It was plugged with cotton wool and the weighed.
- The packed column was rolled into a round-shaped using the steel bar as shown in Photograph 5- 6. The column was fitted in the GC oven for the experimental runs



Photograph 5- 6: Round-shaped column and fitted column in the oven.

Preparation of vials

- The vials were soaked in the 10% solution of nitric acid for 24 hours to remove any contamination.
- The vails were washed with soapy water, rinsed with clean warm water repeatedly. The vails were placed in the oven for drying. All vails were labeled and filled with solutes as presented in the Photograph 5- 7.
- The vails were stored in the fridge, at the controlled temperature and away from light to prevent any evaporation of volatile solutes.



Photograph 5- 7: Solutes vials and the syringe.

With this procedure, the mass of a solvent was determined. Detailed calculation is available in Appendix B.

Retention time

Retention times from the experiments were determined through GC software by calculating the amount of time it takes for each solute to reach the thermal conductivity detector from the injection point. Each signal produced by the thermal conductivity detector was displayed in the form graphs or peaks. Accurate retention times were determined as the from the injection point to the intersection of the tangents to the peak as shown in Figure 5- 1 (Letcher, 1978).

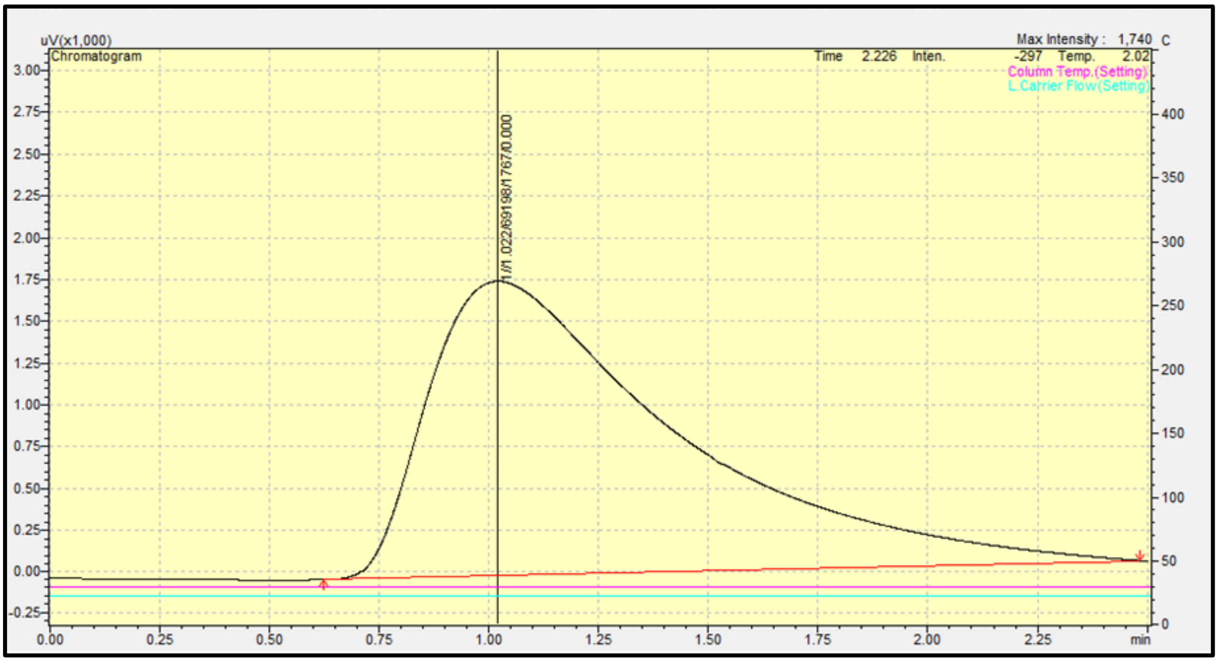
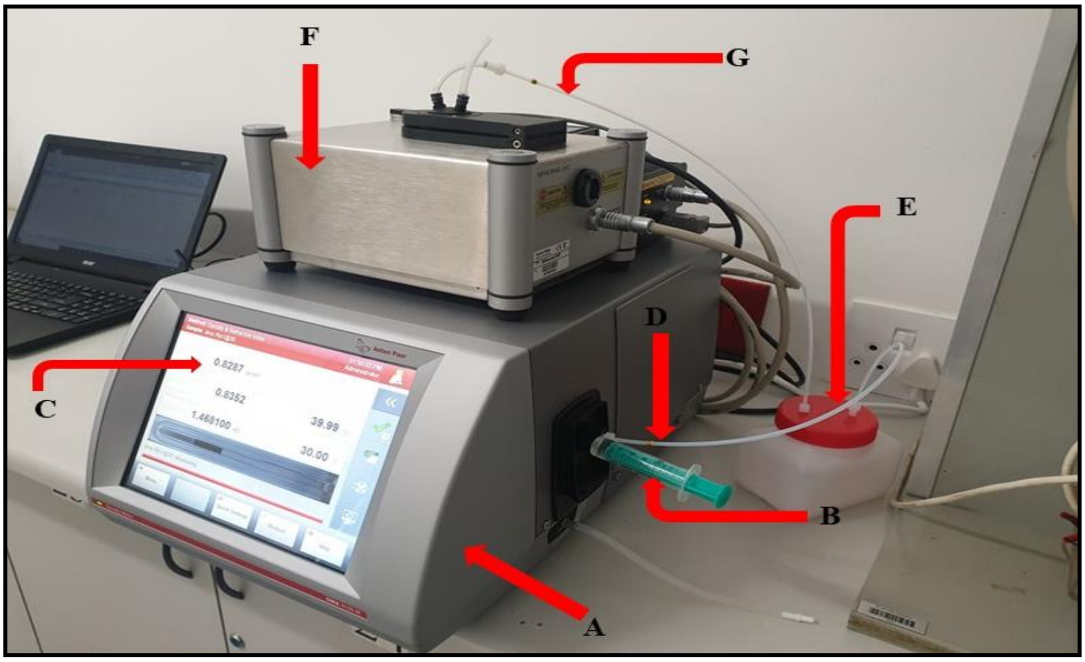


Figure 5- 1: Chromatogram showing detector response vs retention times.

5.3. Refractive index, density, speed of sound and viscosity measurements

5.3.1. Experimental set-up

In this study, the refractive index (n) was measured by using the Anton Paar Refractometer and the density (ρ) using the DMA 4100 M density meter. The Anton Paar refractometer was directly connected to DMA 4100 M for the measurements display as shown in Photograph 5-8. The density meter is fitted with a clear oscillation U-tube for the measurements of the density. Each instrument has its own built-in Peltier thermostat for controlling and maintaining the desired temperature. The speed of sound and viscosity were measured using the Anton Paar oscillation U-tube DSA 5000 M as shown in **Figure 5- 2**.The measurements were determined concurrently, using a single sample.



Photograph 5- 8: Experimental set-up for Anton Paar Refractometer and DMA 4100 M Density meter.

A- DMA 4100 M density meter; B- Syringe feeding to inlet line; C-DMA measurements display; D- Waste line (DMA 4100); E- Waste container; F- Anton Paar refractometer; G- Waste line (Refractometer).

Figure 5- 2 : Photograph for the Anton Paar oscillation U-tube DSA 5000 M.

(Taken from Instruction Manual of Anton Paar DSA 5000 M)

5.3.2. Experimental procedure

Refractive index

The refractive index of the limonene solvent was measured using the Anton Paar Refractometer. The refractometer was connected to the DMA 4100 M instrument for displaying results of refractive indices in the LED screen. The glass prism of the refractometer was cleaned using a soft cloth, to remove any dirt around the prism glass. Prior to the refractive index measurements, the water calibration was done at 298.15 K as presented in Table 5- 2 to ensure that the equipment will produce valid results. Small droplets of the sample were added into the refractometer using the syringe to achieve thin film across the prism and the cap was closed. Both instruments were turned on for measurements, the desired temperature was set on DMA 4100 M, the instrument was allowed to stabilize for a few minutes and the reading was taken. The measurement was repeated three to four times to evaluate the repeatability. The relative deviation (R.D) was found to be less than -0.04%, thus the equipment is more accurate. The detail calculation is presented in chapter 6.

Table 5- 2: Calibration of refractometer using double distilled water at 298.15 K.

Experimental- refractive index	Literature- refractive index	R.D%
1.3325	1.3330[a]	-0.04

[a](Hale and Querry, 1973)

Density meter

The density of limonene was measured using the Anton Paar DMA 4100 M, U-tube densimeter. Before the experimental run, the DMA 4100 M inlet line was flashed with the acetone into the waste container, cleaning and removing any contaminants inside the pipeline and it was allowed to dry. Prior to the density measurements, the water calibration was done at 298.15 K as presented in Table 5- 3 to ensure that the equipment will produce valid results. The syringe filled with the sample was inserted in the inlet line, and it was allowed to flow throughout the pipeline. The bubble formed inside the U-tube pipe was removed by adding more limonene until all bubble were eliminated, and this was done through the camera. The desired temperature was set on the instrument and it was allowed to stabilize. Density results were displayed in the LED screen and the measurement was repeated three to four times to evaluate repeatability. The relative deviation was found to be less than 0.01%, thus the equipment is more accurate.

Table 5- 3: Calibration of density meter using double distilled water at 298.15 K.

Experimental- density g/cm^3	Literature- density g/cm^3	R.D%
0.9971	0.9970[b]	0.01

[b](Bunger and Riddick, 1970)

Speed of sound and viscosity

The speed of sound and viscosity for the limonene were measured using the Anton Paar oscillation U-tube DSA 5000 M. Prior the experimental analysis, ethanol was used to clean the cell, and acetone for drying using the automatic Xsample 452 Module. Prior to the density measurements, the water calibration was done at 298.15 K as presented in Table 5-4 to ensure that the equipment will produce valid results. The vial filled with sample was placed into the Xsample 452. The bubbles formed inside the U-tube pipe were removed by adding more limonene automatically until all bubbles were eliminated, and this was done through the camera. The desired temperature was set on the instrument and it was allowed to stabilize. The speed of sound and viscosity results were displayed in the LED screen and the measurements were repeated three to four times to evaluate repeatability.

Table 5-4: Calibration of Anton Paar oscillation U-tube DSA 5000 M using double distilled water at 298.15 K.

Experimental- viscosity (mPa.s)	Literature- viscosity (mPa.s)	R.D%
0.9110	0.8462[c]	0.01

[c](Whitakeroil., 2018)

Hexadecane test system

The hexadecane test system was selected to confirm the reliability of the experimental set-up and the accuracy of the experimental procedure used in this study. The test system included the n-hexadecane solvent and benzene as a solute at a temperature of 298.15 K.

List of equipment

- Shimadzu GC-2014
- Sartorius vacuum pump
- Oven

- Sartorius analytical balance BSA224S-CW
- Helium gas cylinder
- Bubble flow meter
- DMA 4100 M density meter
- Anton Paar oscillation U-tube DSA 5000 M
- Anton Paar refractometer
- LCD digital air pressure meter SCT-108.001.37
- Round bottom flask
- Rotating stand
- Vails
- Syringes
- Computer

CHAPTER 6

RESULTS AND DISCUSSION

Chapter overview

The chapter represents the results for the hexadecane test system to confirm the reliability and accuracy of the experimental set-up and procedure for this study. The materials used, experimental setup and procedure for the measurements of the activity coefficients are highlighted in this chapter. The experimental results obtained in this study are discussed in this chapter and are compared with the DES, ILs and industrial based solvents for the separation of azeotropic and close boiling point mixtures.

6.1. Chemical used

The chemical used in this study for both the tests system and experimental runs were purchased from different suppliers, local and international as shown in Appendix A. The GLC technique used in this study requires chemicals to have high purity due to its sensitivity and these chemicals are added in small quantities of about $\leq 4\ \mu l$. Chemical used in this study were found to be within the acceptable limit of purity, no pretreatment of chemicals was required.

Two textbooks namely: CRC Handbook of Chemistry and Physics, and the Handbook of Properties of Gas and Liquids (Poling et al., 2000) and (Lide, 2004) were used in the study to source out the properties for the chemicals. These properties are critical temperature, critical pressure, critical volume, acentric factor, ionization potential and constants for vapor pressure correlation. When calculating the infinite dilution activity coefficients, these parameters play a critical role as they characterise the nature of the solutes. The second virial coefficients of pure solutes were calculated using the McGlashan and Potter (1962) Equation (3- 26) as explained in chapter 3.

6.2. Hexadecane test system

The infinite dilution activity coefficient of the test system for the benzene in was measured at the temperature of 298.15 K as shown in Table 6- 1. This was the initial step prior to the experimental runs, this is to ensure that the reliability and accuracy of the equipment and it was compared with the available data on the literature. The experimental data for the test system was found to be 3.09 % which is in line with the literature.

Table 6- 1: Infinite dilution activity coefficient for the test system of benzene in hexadecane at 298.15 K.

Solute	Experimental γ_{13}^{∞}	Literature γ_{13}^{∞}	R.D%
Benzene	1.093	1.060[a]	3.09

[a](Tiegs et al., 1986)

The Equation (6- 1) below was used to calculate the relative deviation. The measurement was initially undertaken and was therefore the prone to error due to the experimental technique. The deviation was found to be minimal between the experimental data and literature and this verified that the GLC method provided the accurate and reliable results.

$$R.D = \frac{\gamma_{13}^{\infty,exp} - \gamma_{13}^{\infty,lit}}{\gamma_{13}^{\infty,lit}} \times 100\% \qquad (6\text{- }1)$$

Three properties were measured for the limonene solvent and were compared with the literature to assess the purity of the solvent. These properties were density, refractive index and viscosity. Table 6- 2 to Table 6- 3 presents the properties of limonene in this study.

Table 6- 2: Density and refractive index at T = 293.15 K for the limonene.

Temperature K	Exp density (ρ) g/cm^3	Lit density (ρ) g/cm^3	Exp refractive index (*n*)	Lit refractive index (*n*)
293.15	0.8440	0.8420[b]	1.4730	1.4730[b]

[b](SigmaAldrich, 2020)

Table 6- 3: Viscosity at T = 298.15 K for the limonene

Temperature	Exp viscosity (μ) mPa.s	Lit viscosity (μ) mPa.s
298.15	0.9110	0.8462

[c](Whitakeroil., 2018)

The density and refractive index were measured at the temperature of 293.15 K, viscosity at the temperature of 298.15 K and were compared with the literature values. Appendix A provides more details for the measurements between 293.15 K to 333.15 K.

6.3. Measurements for the infinite dilution activity coefficients

The results from Table 6- 4 and Table 6- 5 were used to calculate the average infinite dilution activity coefficients values as reported in Table 6- 6. These average values were used to determine the partial excess molar enthalpies at infinite dilution from the temperature dependence, selectivity and capacity at infinite dilution. The focus of this study was to assess the ability to separate mixtures that form azeotropes or have close boiling points. The wide range of polar and non-polar solutes was investigated and it provides new trends to be created with regards to the different classes of solutes. The limonene was used as a solvent in this study and the infinite dilution activity coefficient data presented in this study are new, no data has been presented previously.

Table 6- 4: Experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene at temperature of (303.15 – 333.15) K with the solvent column loading n_3 = 3.867 mmol (27.36%).

Experimental γ_{13}^{∞} at T/K				
Solutes (i)	T=303.15	T=313.15	T=323.15	T=333.15
n-Pentane	33.765	25.425	19.403	14.334
n-Hexane	94.195	67.332	53.247	41.578
n-Heptane	191.602	159.631	128.178	98.577
n-Octane	265.455	228.656	191.557	160.168
n-Nonane	290.743	280.525	253.647	215.858
Hex-1-ene	96.087	75.105	56.778	42.862
Hept-1-ene	161.782	129.363	103.594	81.301
Oct-1-ene	228.983	191.288	153.962	124.764
Non-1-ene	264.094	247.546	214.393	183.294
Dec-1-ene	294.373	286.680	285.967	277.601
Hex-1-yne	112.730	85.224	65.126	49.091
Hept-1-yne	137.204	112.952	95.349	72.663
Oct-1-yne	207.678	178.925	154.046	131.522
Cyclopentane	67.003	50.948	39.759	31.359
Cyclohexane	136.133	106.466	81.334	67.023
Cycloheptane	200.508	172.603	141.565	116.129
Cyclooctane	232.833	215.229	189.397	161.633
Thiophene	112.442	90.984	72.190	56.648
Pyridine	108.655	95.611	80.758	70.865
Ethanol	213.705	163.652	125.266	100.495
Methanol	152.136	113.955	86.781	65.418
Propan-1-ol	245.099	207.204	171.799	144.755
Propan-2-ol	232.289	183.035	144.711	113.987
Butan-1-ol	283.289	235.917	201.326	173.637
Pentan-1-ol	251.707	232.688	217.850	204.872
tert-Butanol	234.361	181.295	137.660	105.210
Benzene	132.202	108.290	83.127	66.782
Toluene	150.244	135.554	116.544	100.421
Ethylbenzene	174.389	168.606	153.293	136.023
m-Xylene	178.245	164.918	150.718	129.131
Acetone	99.057	73.700	59.147	48.630
Butan-2-one	138.264	108.357	85.316	69.589
Pentan-2-one	163.250	137.525	114.151	95.350
Methylacetate	84.629	60.042	44.860	35.611
Ethylacetate	114.710	90.826	67.937	53.637
Acetonitrile	191.990	147.261	114.114	88.045
Water	57.899	43.853	35.089	27.190

Table 6- 5: Experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene at temperature of (303.15 – 333.15) K with the solvent column loading n_3 = 4.939 mmol (33.35%).

	Experimental γ_{13}^{∞} at T/K			
Solutes (i)	T=303.15	T=313.15	T=323.15	T=333.15
n-Pentane	51.136	36.824	24.530	21.504
n-Hexane	114.759	89.317	67.857	51.053
n-Heptane	228.327	173.354	133.203	100.665
n-Octane	324.033	268.177	205.764	157.234
n-Nonane	373.549	345.073	301.005	244.390
Hex-1-ene	103.691	77.114	56.466	42.055
Hept-1-ene	184.129	141.966	108.639	80.395
Oct-1-ene	272.506	216.691	178.285	142.352
Non-1-ene	336.713	284.122	246.328	203.083
Dec-1-ene	373.709	289.253	277.056	244.076
Hex-1-yne	94.204	75.664	62.235	53.690
Hept-1-yne	138.150	116.092	98.756	91.409
Oct-1-yne	182.142	164.673	145.047	131.707
Cyclopentane	73.072	58.767	45.440	36.635
Cyclohexane	148.681	118.189	90.760	69.558
Cycloheptane	224.668	195.152	156.929	130.069
Cyclooctane	271.921	249.163	215.983	181.658
Thiophene	104.457	90.452	75.450	64.707
Pyridine	65.628	61.738	56.525	53.837
Ethanol	154.990	130.849	109.510	89.322
Methanol	118.862	92.952	72.624	59.032
Propan-1-ol	165.220	149.519	134.481	115.979
Propan-2-ol	171.042	144.198	120.730	101.406
Butan-1-ol	186.976	180.056	154.984	132.583
Pentan-1-ol	170.607	161.154	156.652	148.462
tert-Butanol	191.518	154.146	119.494	95.171
Benzene	125.595	103.328	83.005	66.227
Toluene	143.654	128.270	112.564	97.224
Ethylbenzene	172.214	163.378	149.261	133.573
m-Xylene	182.145	167.408	152.085	136.034
Acetone	88.918	71.390	57.145	45.515
Butan-2-one	121.180	102.048	83.600	68.698
Pentan-2-one	135.003	119.730	103.177	88.173
Methylacetate	85.051	63.557	49.904	41.011
Ethylacetate	108.588	91.957	72.498	61.480
Acetonitrile	201.259	147.393	113.012	92.008
Water	47.040	40.079	30.618	24.322

Table 6- 6: Average experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene at temperature of (303.15 – 333.15) K.

	Experimental γ_{13}^{∞} at T/K			
Solutes (i)	T=303.15	T=313.15	T=323.15	T=333.15
n-Pentane	42.450	31.124	21.967	17.919
n-Hexane	104.477	78.324	60.552	46.316
n-Heptane	209.964	166.492	130.690	99.621
n-Octane	294.744	248.417	198.660	158.701
n-Nonane	332.146	312.799	277.326	230.124
Hex-1-ene	99.889	76.110	56.622	42.458
Hept-1-ene	172.956	135.665	106.117	80.848
Oct-1-ene	250.745	203.989	166.124	133.558
Non-1-ene	300.403	265.834	230.360	193.188
Dec-1-ene	334.041	287.966	281.511	260.838
Hex-1-yne	103.467	80.444	63.681	51.390
Hept-1-yne	137.677	114.522	97.052	82.036
Oct-1-yne	194.910	171.799	149.546	131.615
Cyclopentane	70.038	54.857	42.599	33.997
Cyclohexane	142.407	112.327	86.047	68.291
Cycloheptane	212.588	183.877	149.247	123.099
Cyclooctane	252.377	232.196	202.690	171.646
Thiophene	108.449	90.718	73.820	60.677
Pyridine	87.142	78.674	68.641	62.351
Ethanol	184.348	147.251	117.388	94.909
Methanol	135.499	103.453	79.702	62.225
Propan-1-ol	205.159	178.362	153.140	130.367
Propan-2-ol	201.666	163.616	132.720	107.696
Butan-1-ol	235.132	207.987	178.155	153.110
Pentan-1-ol	211.157	196.921	187.251	176.667
tert-Butanol	212.940	167.720	128.577	100.190
Benzene	128.898	105.809	83.066	66.504
Toluene	146.949	131.912	114.554	98.822
Ethylbenzene	173.302	165.992	151.277	134.798
m-Xylene	180.195	166.163	151.402	132.582
Acetone	93.988	72.545	58.146	47.073
Butan-2-one	129.722	105.202	84.458	69.143
Pentan-2-one	149.127	128.628	108.664	91.762
Methylacetate	84.840	61.799	47.382	38.311
Ethylacetate	111.649	91.392	70.218	57.559
Acetonitrile	196.625	147.327	113.563	90.027
Water	52.470	41.966	32.854	25.756

6.4. Effect of molecular structure on IDACs values

Alkanes

Alkanes are saturated hydrocarbons, containing a single bond. This means that each carbon has a maximum number of hydrogens bonded attached to it. There is little difference in electronegativity between the carbon and hydrogen, therefore they are considered as non-polar molecules due to the negligible dipole moments that they possess. Alkanes are often referred to as aliphatic hydrocarbons because of the physical properties and long carbon chain that they can form. The only van der Waals forces that can operate in the alkane interactions are London dispersion forces. They are highly unreactive when compared to double and triple bond hydrocarbons.

The results from Figure 6- 1 indicates that the activity coefficient values increase with the increase in alkyl chain length. This is attributed to the London forces that are acting between alkane molecules. As the electrons move further and further away from the nucleus due to the increase of alky chain length or solute structural size, the intermolecular forces acting between the solute-solute increases in such a way that it becomes difficult for the limonene solvent to break these forces that are existing between the solute-solute as to form new solute-solvent bonds. This increases the energy required to break the cohesive forces between the solute molecules before intermolecular bonding with the solvent that can take place, therefore the increase in activity coefficients with an increase of alkyl chain length. The non-polar solute with the small alkyl chain length will have weak dispersion forces, and the electron cloud of the solvent will easily overcome the small electron cloud of the solute consequently inducing a temporary dipole. This has resulted in the low values of activity coefficients; hence the solute is easily absorbed by the solvent. The lower values of activity coefficients also imply greater solubility. It is observed that as the temperature increases the solubility increase, meaning that as more energy is added into the system the better the solubility. The intermolecular forces are broken down easily when the temperature is increased.

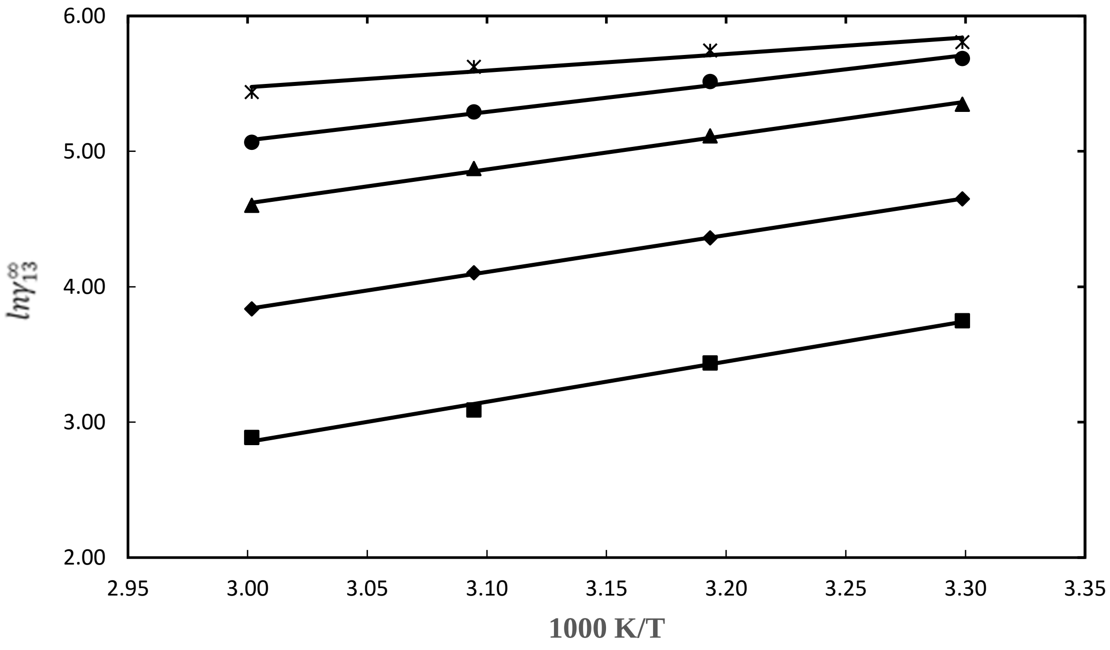


Figure 6- 1: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: n-pentane (■); n-hexane (♦), n-heptane (▲), n-octane (●), n-nonane (✳) in Limonene.

Alkenes

The activity coefficient values were determined for the 5 alkenes on the limonene solvent in this work. The alkenes contain carbon bonded to hydrogen atoms; alkanes contain double bonded carbon which makes them olefinic (unsaturated) in nature. They are classified as non-polar molecules due to carbon and hydrogen atoms and therefore van der Waal forces that can operate in alkene interactions are London dispersion forces.

Figure 6- 2 shows that for the alkene there is a trend of increasing activity coefficients with the increase of alkyl chain length. The increase in activity coefficients with an increase in alkyl chain length was caused by solute size since no chemical reaction occurs. As the non-polar solute increases its molecular size, the surface area also increases increasing the strength of the London forces of the solute-solute. When compared with alkanes, the alkenes yielded lower values of activity coefficients. It should be noted that the alkanes have higher boiling points than alkenes with a similar structure and number of carbons. The strength of solute-solute intermolecular forces for the alkanes are higher than those of alkenes. This could be attributed to the fact that the alkenes molecules are packed loosely together, creating a less effective surface area between solute-solute bonds for London forces to function. Alkenes are considered

to be more polarised than alkanes due to the combination of one sigma bond and one pi bond. The alkanes only consist of sigma bonds, which create a strong carbon-carbon bond and it is supported by high values of experimental activity coefficients when compared with alkenes.

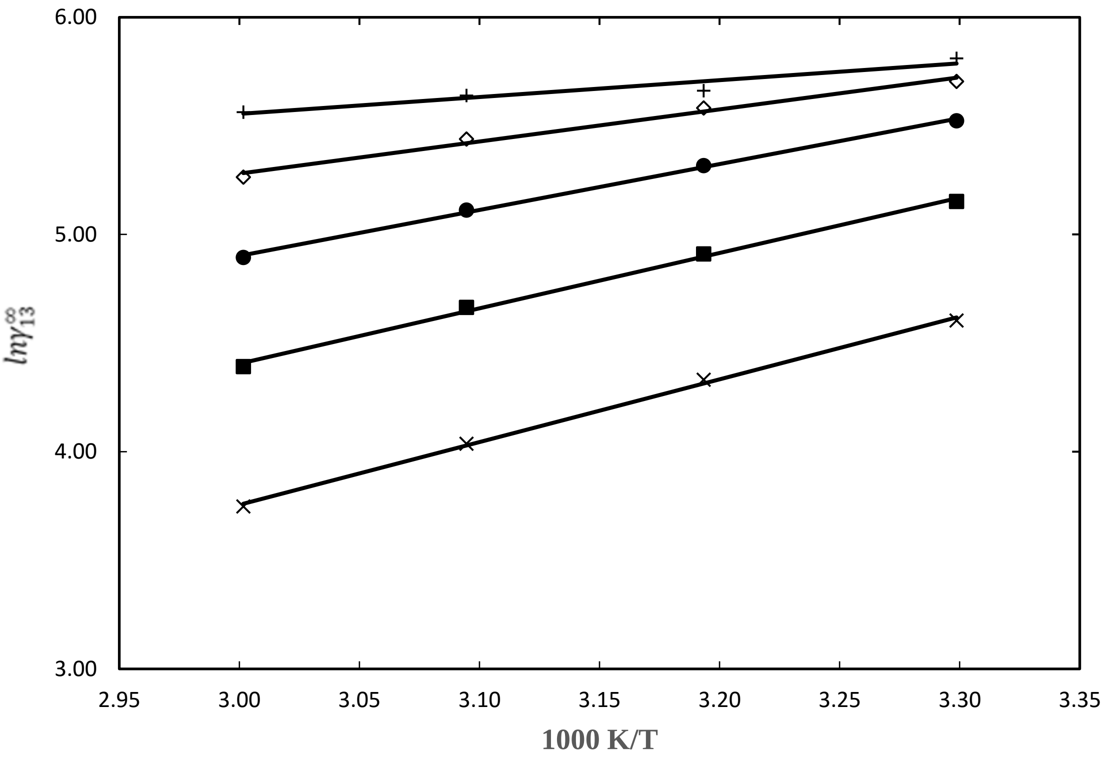


Figure 6- 2: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: hex-1-ene (×), hept-1-ene (■), oct-1-ene (●), non-1-ene (◊), dec-1-ene (+) in Limonene.

Alkynes

The activity coefficient values were determined for the 3 alkynes on the limonene solvent in this work. Alkynes are non-polar unsaturated hydrocarbons and are dominated by London dispersion forces. The triple bond contributed to the non-polar bonding strength. In Figure 6-3 it is observed that the activity coefficients increase with the increase of alkyl chain length. This trend was similar for the alkanes and alkenes. This is attributed to the high polarisation of the triple bond between carbon-carbon atoms. Alkynes are more polarised than alkenes and alkanes due to the electrons constituting the double pi bonds that are not confined to the regions around the centers of the two carbon atoms which create the triple bond. The triple bond creates strong interaction between the solute-solute than the alkenes. Alkynes are linear in structure; this permits for closer packing of the solute molecules with each other than alkenes thus enhancing the strength of London forces. The alkynes are more reactive than alkanes due to the one sigma bond and two pi bonds between the carbon atoms. The pi electrons are more open to attack by other molecules than the sigma bond which are located within the protected space between atom, resulting in strong interaction. Therefore, lower values of activity coefficients were observed.

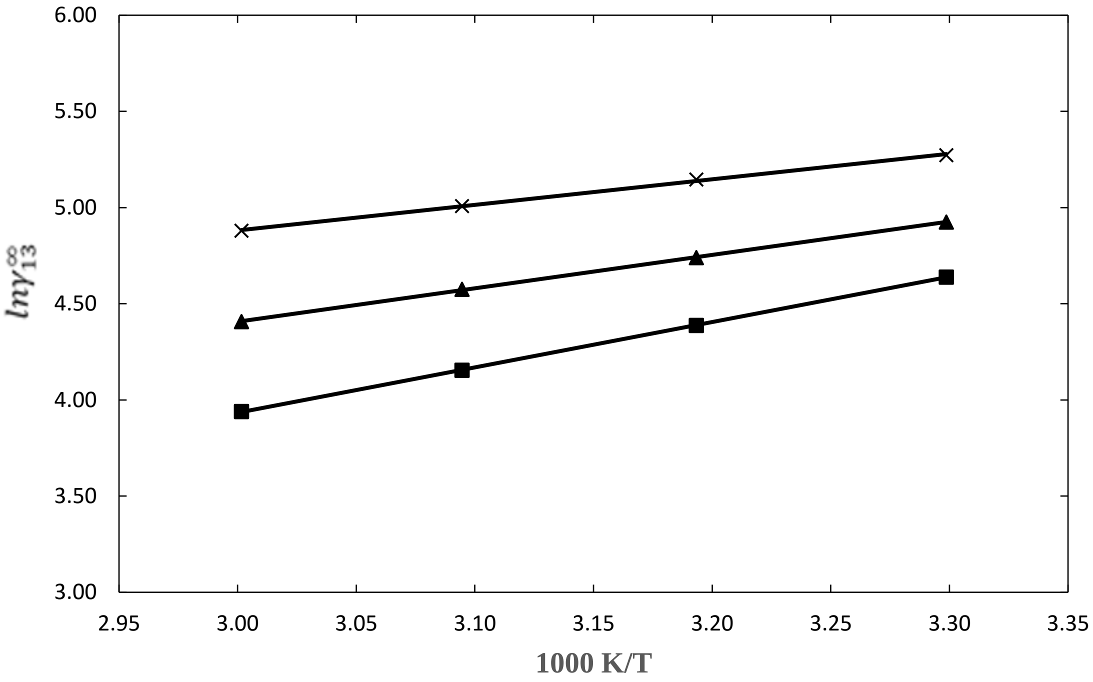


Figure 6- 3: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: hex-1-yne (■), hept-1-yne (▲), oct-1-yne (×) in Limonene.

Cycloalkanes

Cycloalkanes consist of carbon and hydrogen atoms that are saturated because of a single carbon-carbon bond. They are classified as non-polar hydrocarbon molecules due to their low values of electronegativity between carbon and hydrogen atom. Cycloalkanes are similar to alkanes because of the single C-H bond; however, the only difference is that cycloalkanes have higher boiling points than alkanes when compared with the same carbon number. Therefore, cycloalkanes are non-polar hydrocarbons and there is only weak interaction between their molecules. Figure 6- 4 illustrates a clear trend of increasing the activity coefficient values with an increase of alkyl chain length. This is due to the increase of effective surface area of the cycloalkane, increasing the strength of the London forces for solute molecules. As the electrons move further and further away from the nucleus due to the increase of molecule size, more energy is required to break the solute-solute bond. This explains the steady increase of activity coefficient values for the cycloalkanes. Furthermore, it was observed that the activity coefficient values for cycloalkanes are higher when compared with alkanes. This is due to the fact that cycloalkanes have higher London dispersion forces because of the ring shape allows for greater area contact, thus making the bond difficult to break.

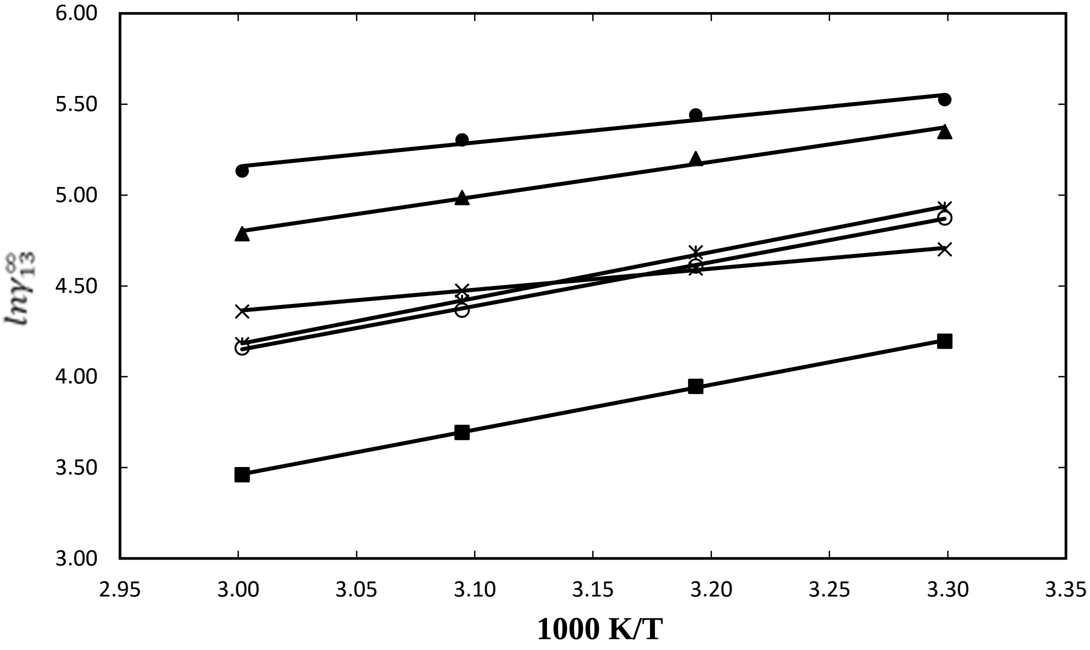


Figure 6- 4: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: cyclopentane (■), cyclohexane (✳), cycloheptane (▲), cyclooctane (●), Thiophene (○), Pyridine (×) in limonene.

Heterocyclic

Heterocyclics are organic compounds with the ring structure that contains in the cycle at least one carbon atom and one other element such as nitrogen, oxygen and sulphur. The interaction of heterocyclic compounds namely pyridine and thiophene were investigated in this work. Pyridine molecule contains a ring of six-atoms, five carbon atoms and one nitrogen atom. Thiophene molecule contains a ring of five-atoms, four carbon atoms and one sulphur atom. Pyridine and thiophene are classified as unsaturated hydrocarbons due to the double bond that they contain between any two carbon atoms. Figure 6- 4 illustrates that the activity coefficients of thiophene are higher than those of the pyridine and this is due to molecular structure. Thiophene has higher electronegativity as compared to pyridine due to the presence of sulphur atom, resulting in an increase of the strength of the London forces of the solute-solute. This is supported by the higher values of activity coefficients for thiophene as compared to the lower values for pyridine. These lower values for pyridine symbolise strong molecular interaction with the solvent.

Aromatics

Infinite dilution activity coefficients of 4 aromatic hydrocarbons were calculated. Aromatics are unsaturated non-polar hydrocarbons containing one or more rings. Benzene is the simplest and most stable aromatics. The aromatics contain sigma and delocalised pi bonds between carbon atoms. Alkylbenzene such as toluene, ethylbenzene and m-xylene are investigated in this work. From Figure 6- 5 it can be observed that the activity coefficients increase with the increase of alkyl chain. This is caused by the delocalised pi electrons around six hydrogen atoms which form the electron cloud above and below the benzene ring. The attachment of methyl group on the benzene structure increases the strength of London dispersion forces as the carbon in the methyl group is electron donating, thus making the ring to have greater electron density.

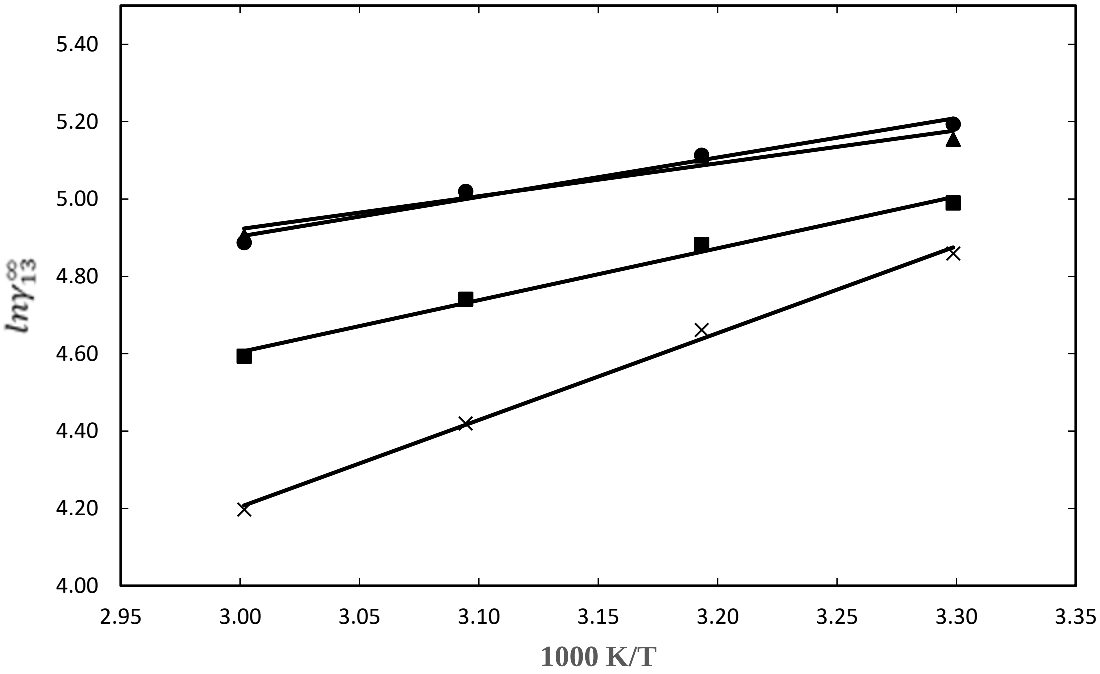


Figure 6- 5: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: benzene (×), toluene (■), ethylbenzene (▲), m-xylene (●) in Limonene.

Alcohols

Alcohols are seen by their hydroxyl (-OH) functional group. They are classified as polar molecules due to the high electronegativity between the oxygen and hydrogen atom in the hydroxyl group, as a result, they actively participate in the hydrogen bonding. The activity coefficients for the alcohols increases with the increase of alkyl chain as shown in Figure 6- 6. This is due to the strong intermolecular forces between the solute molecules, as the alkyl chain increases its size, the electrons move further away from the nucleus and resulting strong hydrogen bond between the solute molecules. Therefore, as the alkyl chain increases its size more energy is required to break solute-solute bonds as for the new solute-solvent bonds to be formed. Hence high activity coefficients are observed for the higher alkyl chain size. Furthermore, it is observed that the activity coefficient decreases as the alcohol molecule branches. This is attributed to the decrease of the surface area around the branched molecule, thereby decreasing the attractive force between the molecules, as a result, the branched alcohol molecule will have low values of infinite dilution activity coefficients that the straight chain molecules.

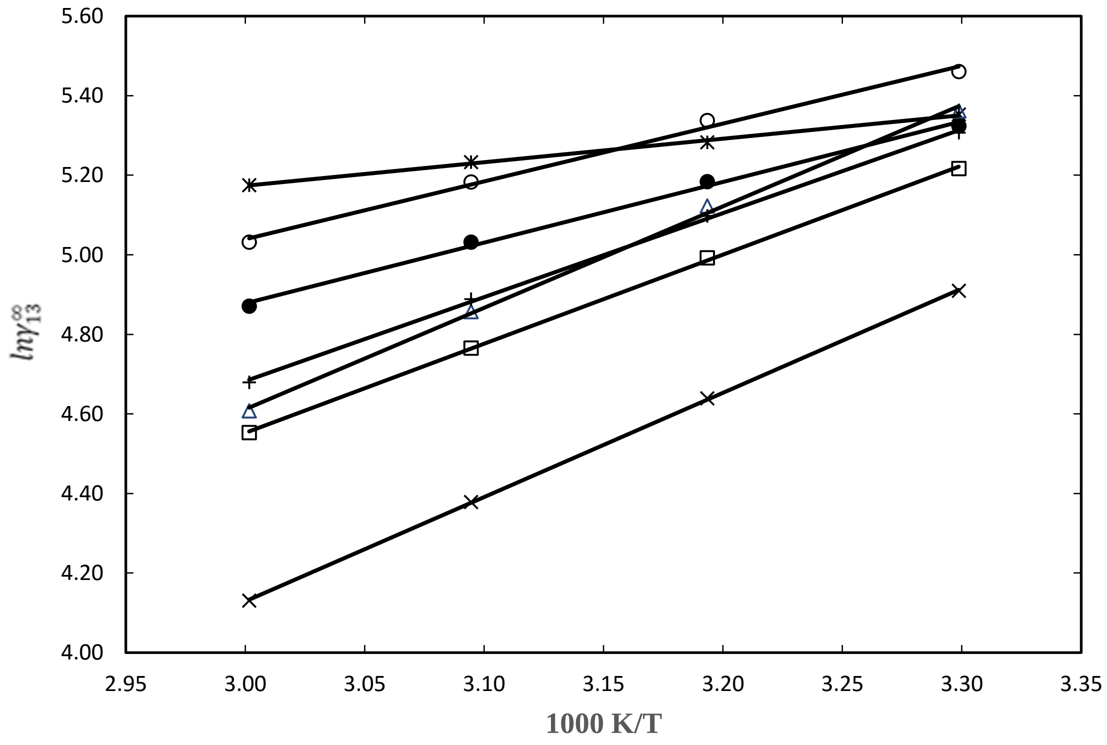


Figure 6- 6: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: methanol (×), ethanol (■), propan-1-ol (●), propan-2-ol (+), butan-1-ol (●), pentan-1-ol (✻), tetr-butanol (▲) in Limonene.

Ketones

Ketones are classified as organic compounds characterised by the presence of a carboxyl functional group whereby the carbon atom is bonded to an oxygen atom. Ketones are polar in nature, due to the high electronegativity between the carbon atom and oxygen atom, thus dipole-dipole forces will operate between the molecules. From Figure 6- 7 it can be seen that the infinite dilution activity coefficients of the 3 ketones increase with an increase in the ketone chain length. This is attributed to the increase of dipole-dipole forces between the solute molecules, thus reducing the interaction between the solute and solvent. Dipole-dipole forces are stronger than the London forces and it is for this reason the ketones will have higher activity coefficients that the alkane when compared with the same carbon number.

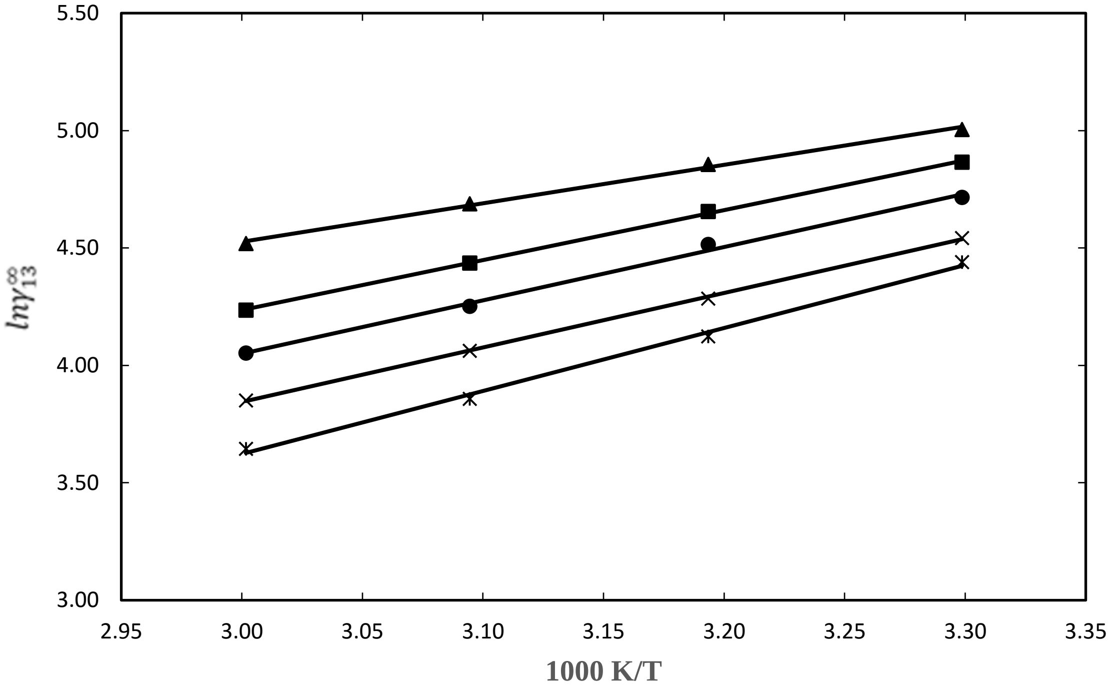


Figure 6- 7: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: methylacetate (✳), acetone (×), ethylacetate (●), butan-2-one (■), pentan-2-one (▲) in Limonene.

Ethers

Ethers are classified as organic compounds that contain oxygen between two alkyl group. Ethers are non-polar in nature; this is due to the electronegativity between the oxygen and carbon atom. The presence of alkyl groups on both sides of the oxygen atoms, it enables the oxygen atom to participate in the hydrogen bonding, thus dipole-dipole will operate between the molecules. From Figure 6- 8 it was observed that the activity coefficients increase with the increase of alkyl chain. This is due to the effect of an increase in dipole-dipole forces as the number of carbon increases thus the number of electrons increases. The high values of activity coefficient for the ethers represent the strong intermolecular forces between the solute molecules. When compared with the alcohols, with the same number of carbons, it was observed that the ethers have a lower activity coefficient because they can only form dipole-dipole forces which are supported by the low values of activity coefficient.

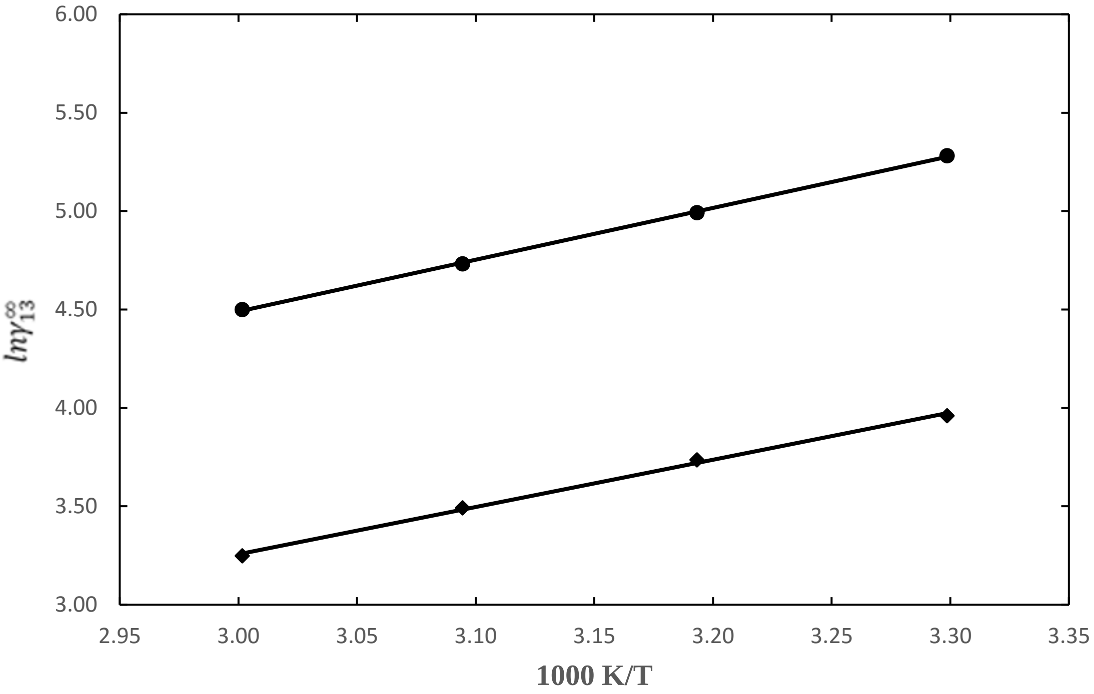


Figure 6- 8: Plots of ln (γ_{13}^{∞}) against 1/T for the solutes: acetonitrile (●) and water (♦) in Limonene.

Water

Water is classified as a polar molecule that consists of two hydrogen atoms and one oxygen atom. Water is highly polar due to the high electronegativity of the hydroxyl oxygen atom. This is due to the high electronegativity of the oxygen atom that is bonded to the hydrogen atom hence they can actively participate in the hydrogen bond both as hydrogen donor and acceptor.

Since the limonene solvent is non-polar, thus possessing weak London forces. This creates weak interaction between solute and solvent. The hydrogen bond existing between solute-solute molecules creates a strong force of attraction in such a way that it becomes difficult for the new solute-solvent bond to be formed, resulting in poor solubility. Figure 6- 8 illustrates that the activity coefficients increase with the increase in temperature.

6.5. Partial molar excess enthalpy at infinite dilution

The experimental infinite dilution activity coefficients were measured at temperatures between 303.15 K - 333.15 K. The partial molar excess enthalpy at infinite were determined from the temperature dependency of $\ln\gamma_{13}^{\infty}$ against the temperature by using Gibbs-Helmholtz Equation (3- 8) and the results are reported in

Table 6- **7**. The logarithm of activity coefficients values as a function of inverse temperature for solutes as presented on Figure 6- 1 to Figure 6- **8** reveals the possibility of determining the activity coefficient at any given temperature through interpolation.

The partial molar excess enthalpies at infinite were used to evaluate the molecular interaction between the solute-solute and solute-solvent interaction. The positive values for the enthalpies were observed for all the solutes in the limonene solvent. These positive $\Delta H_1^{E,\infty}$ values imply that the activity coefficient decreases with the increase of temperature. This indicates that the solubility increases with the temperature increase. Furthermore, positive values of $\Delta H_1^{E,\infty}$ also indicate that the interaction between the solute-solute pairs is lower than the solute-solvent pairs and that the solutes possess an endothermic heat of mixing when contacted with the solvent.

Table 6- 7: The partial excess enthalpy at infinite dilution for various solutes obtained from the Gibbs-Helmholtz equation.

Solutes (i)	a	b (K)	γ_{13}^{∞} (313.15 K)	$\Delta H_1^{E,\infty}$ (kJ.mol^{-1})	R^2
n-Pentane	2.970	-6.056	31.124	24.693	0.993
n-Hexane	2.724	-4.336	78.324	22.650	1.000
n-Heptane	2.500	-2.882	166.492	20.781	0.996
n-Octane	2.097	-1.209	248.417	17.433	0.992
n-Nonane	1.225	1.800	312.799	10.181	0.936
Hex-1-ene	2.888	-4.909	76.110	24.012	0.998
Hept-1-ene	2.549	-3.241	135.665	21.191	0.997
Oct-1-ene	2.114	-1.440	203.989	17.575	0.998
Non-1-ene	1.478	0.847	265.834	12.287	0.988
Dec-1-ene	0.777	3.226	287.966	6.457	0.920
Hex-1-yne	2.357	-3.138	80.444	19.598	1.000
Hept-1-yne	1.736	-0.801	114.522	14.432	1.000
Oct-1-yne	1.329	0.895	171.799	11.048	0.999
Cyclopentane	2.445	-3.812	54.857	20.328	1.000
Cyclohexane	2.495	-3.261	112.327	20.741	0.999
Cycloheptane	1.862	-0.762	183.877	15.481	0.991
Cyclooctane	1.299	1.270	232.196	10.802	0.971
Thiophene	1.965	-1.785	90.718	16.340	0.997
Pyridine	1.152	0.674	78.674	9.575	0.995
Ethanol	2.240	-2.167	147.251	18.623	1.000
Methanol	2.621	-3.735	103.453	21.792	1.000
Propan-1-ol	1.526	0.301	178.362	12.684	0.997
Propan-2-ol	2.111	-1.650	163.616	17.548	0.999
Butan-1-ol	1.453	0.679	207.987	12.084	0.994
Pentan-1-ol	0.592	3.399	196.921	4.919	0.998
tert-Butanol	2.551	-3.040	167.720	21.205	0.998
Benzene	2.247	-2.535	105.809	18.677	0.996
Toluene	1.341	0.581	131.912	11.152	0.991
Ethylbenzene	0.850	2.373	165.992	7.066	0.953
m-Xylene	1.020	1.844	166.163	8.478	0.979
Acetone	2.302	-3.116	72.545	19.139	1.000
Butan-2-one	2.128	-2.147	105.202	17.688	1.000
Pentan-2-one	1.639	-0.392	128.628	13.629	0.997
Methylacetate	2.682	-4.424	61.799	22.299	0.996
Ethylacetate	2.272	-2.767	91.392	18.892	0.996
Acetonitrile	2.632	-3.406	147.327	21.881	1.000
Water	2.401	-3.945	41.966	19.958	0.998

6.6. Partial activity coefficient

The gas-liquid partial activity coefficients, K_L for solutes in the limonene solvent are listed in Table 6- 8. The densities were taken between the temperatures of 303.15 K to 333.15 K as presented in Table 2. The highest value at T= 313.15 K was observed for dec-1-ene, K_L = 84.842 and the lowest for acetone, K_L = 4.161. It was observed that the values of KL decrease with the increase of temperature, and K_L values increases with the increase of alky chain length.

Table 6- 8: Experimental (gas and liquid) partition coefficients K_L for the solutes in the limonene solvents at temperature of (303.15 – 333.15) K.

Solutes (i)	303.15 K	313.15 K	323.15 K	333.15 K
n-Pentane	4.908	4.832	5.015	4.829
n-Hexane	6.320	5.830	5.294	4.993
n-Heptane	10.161	8.258	7.015	6.270
n-Octane	21.102	15.379	12.208	9.991
n-Nonane	54.667	33.768	23.081	17.348
Hex-1-ene	5.597	5.100	4.922	4.966
Hept-1-ene	9.796	8.241	7.203	6.712
Oct-1-ene	20.129	15.724	12.577	10.451
Non-1-ene	50.806	33.926	23.899	18.197
Dec-1-ene	154.063	84.842	51.177	34.669
Hex-1-yne	7.260	6.381	5.547	4.821
Hept-1-yne	15.133	11.674	9.103	7.415
Oct-1-yne	34.349	23.601	17.025	12.532
Cyclopentane	4.938	4.473	4.169	3.876
Cyclohexane	7.694	6.529	5.892	5.224
Cycloheptane	20.528	14.996	12.126	9.907
Cyclooctane	63.443	40.010	27.662	20.437
Thiophene	11.257	9.005	7.645	6.492
Pyridine	72.890	51.199	40.031	32.323
Ethanol	7.671	5.822	4.617	3.754
Methanol	5.505	4.525	3.824	3.279
Propan-1-ol	17.716	11.702	8.163	5.976
Propan-2-ol	8.821	6.499	4.984	3.933
Butan-1-ol	54.048	29.448	17.845	11.709
Pentan-1-ol	168.603	83.364	44.298	25.758
tert-Butanol	9.778	7.004	5.455	4.390
Benzene	9.139	7.343	6.238	5.469
Toluene	21.767	15.981	12.389	9.875
Ethylbenzene	50.903	32.714	23.043	17.226
m-Xylene	58.256	38.203	26.415	19.652
Acetone	4.615	4.161	3.677	3.309
Butan-2-one	8.484	6.878	5.837	5.007
Pentan-2-one	16.066	12.052	9.593	7.877
Methylacetate	5.349	5.068	4.703	4.198
Ethylacetate	8.989	7.248	6.489	5.560
Acetonitrile	5.655	4.944	4.434	3.938
Water	72.890	51.199	40.031	32.323

6.7. Limiting selectivity and capacity of limonene solvent

The values for the limiting selectivity and capacity were determined by using the experimental measured values of infinite dilution activity coefficients. The selectivity and capacity were calculated using Equation (3- 3) and (3- 4). These factors are useful when it comes to the evaluation of the solvent's performance in the separation processes. Table 6- 9 to Table 6- 15 presents both the selectivities and capacities for the limonene and other ionic liquid solvents for comparison at the temperature of 313.15 K.

n-hexane (*i*) and hex-1-ene (*j*) separation problem

The selectivity and capacity of the limonene for the n-hexane (*i*) hex-1-ene (*j*) separation problem was compared with ILs at the temperature of 313.15 K as listed in Table 6- 9. It was observed that the selectivity for the limonene was above 1, which indicates that the solvent has potential to separate. However, it must be noted that the limonene has the lowest selectivity when compared with ILs and it indicates poor performance for the separation of n-hexane (*i*) and hex-1-ene (*j*). The capacity for the limonene was extremely low but higher than that of DES 1. This implies that more solvent must be added as to achieve the separation and as a result it will increase the running costs since more energy will be used on pumping the solvent

Table 6- 9: A comparison of the selectivity and capacity of solvents for n-hexane (*i*) and hex-1-ene (*j*) separation mixture at the temperature of 313.15 K *[1]This work; [2](Nkosi et al., 2018a); [3](Nkosi et al., 2018b); [4](Domańska and Marciniak, 2009); [5](Domańska and Laskowska, 2009); [6](Paduszyński and Domańska, 2013); [7](Krummen and Gmehling, 2004); [a]interpolate*

	Selectivity ($S_{ij,s}^{\infty}$)	**Capacity ($K_{j,s}^{\infty}$)**
Solvent	**n-hexane(*i*)/hex-1-ene(*j*)**	**hex-1-ene(*j*)**
Limonene, [1]	1.22	0.013
DES 1; ($C_4H_{12}NCl$) :(EG) [1:2],[2]	3.04	0.0017
DES 2; [$4C_1NCl$] + [Gly] [1:2],[3]	0.78	0.004
[$C_6H_{13}OCH_2MIM$] [NTf_2][a],[4]	1.42	0.460
[BMIM][SCN][a],[5]	3.39	0.019
[C_5C_1Pip] [NTf_2][a],[6]	1.79	0.185
[C_6C_1Pip] [NTf_2][a],[6]	1.68	0.223
NMP + 3% (w/w) water,[7]	1.97	0.102
NFM+ 3% (w/w) water,[7]	2.15	0.040

n-heptane (*i*) and benzene (*j*) separation problem

The selectivity and capacity of the limonene for the n-heptane (*i*) and benzene (*j*) separation problem was compared with ILs at the temperature of 313.15 K as listed in Table 6- 10. The values for the selectivity and capacity listed in Table 6- 10 shows that limonene has the lowest values in both factors. This is a clear indication that it has poor performance when compared with ILs, however, it has the potential to separate n-heptane (*i*) and benzene (*j*) mixture since its selectivity is above the one. More solvent will be required to achieve separation.

Table 6- 10: A comparison of the selectivity and capacity of solvents for n-heptane (*i*) and benzene (*j*) separation mixture at the temperature of 313.15 K

[1]This work; [2](Nkosi et al., 2018a); [3](Nkosi et al., 2018b); [4](Nkosi et al., 2019); [5](Domańska and Marciniak, 2009); [6](Domańska and Laskowska, 2009); [7](Paduszyński and Domańska, 2013); [8](Krummen and Gmehling,

	Selectivity ($S^{\infty}_{ij,s}$)	**Capacity ($K^{\infty}_{j,s}$)**
Solvent	**n-heptane(*i*)/benzene(*j*)**	**benzene(*j*)**
Limonene, [1]	1.6	0.010
DES 1; (C$_4$H$_{12}$NCl) :(EG) [1:2],[2]	79.32	0.051
DES 2; [4C$_1$NCl] + [Gly] [1:2],[3]	33.96	0.018
DES 3; [4C$_1$NCl] + [Hdiol] [1:1],[4]	31.74	0.813
[C$_6$H$_{13}$OCH$_2$MIM] [NTf$_2$][a],[5]	6.16	1.646
[BMIM][SCN][a],[6]	106.2	0.463
[C$_5$C$_1$Pip] [NTf$_2$][a],[7]	18.58	1.430
[C$_6$C$_1$Pip] [NTf$_2$][a],[7]	14.76	1.475
NMP + 3% (w/w) water,[8]	16.93	0.714
NFM+ 3% (w/w) water,[8]	26.67	0.358
[PMMIM][NTf$_2$][9]	3.74	0.813
Sulfolane][10]	24.05	0.424

2004); [9](He et al., 2020); [10](Möllmann and Gmehling, 1997); [a]interpolate

Ethanol (*i*) and water (*j*) separation problem

The selectivity and capacity of the limonene for the ethanol (*i*) and water (*j*) separation problem were compared with ILs at the temperature of 313.15 K as listed in Table 6- 11. From Table 6-11 it can be seen that the limonene provides the highest selectivity. This indicates that limonene can be used to separate the azeotropic mixture of ethanol (*i*) and water (*j*). However, it was observed that limonene has the lowest capacity for water. The economics around this separation must be considered carefully. A good solvent must possess high selectivity and capacity.

Table 6- 11: A comparison of the selectivity and capacity of solvents for ethanol (*i*) and water (*j*) separation mixture at the temperature of 313.15 K

[1]This work; [2](Domańska and Marciniak, 2009); [3](Paduszyński and Domańska, 2013); [4](Möllmann and Gmehling, 1997); [a]interpolate

	Selectivity ($S_{ij,s}^{\infty}$)	**Capacity ($K_{j,s}^{\infty}$)**
Solvent	**ethanol (*i*)/water (*j*)**	**water (*j*)**
Limonene, [1]	3.51	0.024
[$C_6H_{13}OCH_2MIM$] [NTf_2][a],[2]	0.39	1.375
[C_5C_1Pip] [NTf_2][a],[3]	0.36	0.593
[C_6C_1Pip] [NTf_2][a],[3]	0.35	0.581
[Sulfolane][4]	1.08	0.355

n-octane (*i*) and pyridine (*j*) separation problem

The selectivity and capacity of the limonene for the n-octane (*i*) and pyridine (*j*) separation problem was compared with ILs at the temperature of 313.15 K as listed in Table 6- 12. The results from Table 6- 12 for n-octane (*i*) and pyridine (*j*) separation problem are not satisfactory when compared with other solvents, low values of selectivity and capacity for the limonene solvent are observed.

Table 6- 12: A comparison of the selectivity and capacity of solvents for n-octane (*i*) and pyridine (*j*) separation mixture at the temperature of 313.15 K

[1]This work; [2](Nkosi et al., 2018b); [3](Nkosi et al., 2019)

	Selectivity ($S_{ij,s}^{\infty}$)	**Capacity ($K_{j,s}^{\infty}$)**
Solvent	**n-octane (*i*)/pyridine (*j*)**	**pyridine (*j*)**
Limonene, [1]	2.48	0.010
DES 2; [$4C_1$NCl] + [Gly] [1:2],[2]	342.81	1.618
DES 3; [$4C_1$NCl] + [Hdiol] [1:1],[3]	556.29	4.717

n-octane (*i*) and thiophene (*j*) separation problem

The selectivity and capacity of the limonene for the n-octane (*i*) and thiophene (*j*) separation problem were compared with ILs at the temperature of 313.15 K as listed in Table 6- 13. The selectivity value for the limonene presented in Table 6- 13 indicates that limonene would perform poorly as a solvent for the separation of n-octane (*i*) and thiophene (*j*) due to its low value. It was observed that the selectivity was greater than one, which indicates that it has the potential to be used for desulfurization of the liquid fuel. The separation would require high quantities of limonene, hence operating costs will be high.

Table 6- 13: A comparison of the selectivity and capacity of solvents for n-octane (*i*) and thiophene (*j*) separation mixture at the temperature of 313.15 K

[1]This work;[2](Nkosi et al., 2018b); [3](Nkosi et al., 2019); [4](Domańska and Marciniak, 2009); [5](Domańska and Laskowska, 2009); [6](Paduszyński and Domańska, 2013); [a]interpolate

	Selectivity ($S_{ij,s}^{\infty}$)	**Capacity ($K_{j,s}^{\infty}$)**
Solvent	**n-octane (*i*)/thiophene (*j*)**	**thiophene (*j*)**
Limonene, [1]	2.44	0.010
DES 2; [4C$_1$NCl] + [Gly] [1:2],[2]	81.8	0.386
DES 3; [4C$_1$NCl] + [Hdiol] [1:1],[3]	154	1.307
[C$_6$H$_{13}$OCH$_2$MIM] [NTf$_2$][a],[4]	7.91	1.745
[BMIM][SCN][a],[5]	236.28	0.801
[C$_5$C$_1$Pip] [NTf$_2$][a],[6]	28.22	1.608
[C$_6$C$_1$Pip] [NTf$_2$][a],[6]	20.63	1.612

n-octane (*i*) and ethyl acetate (*j*) separation problem

The selectivity and capacity of the limonene for the n-octane (*i*) and ethyl acetate (*j*) separation problem were compared with ILs at the temperature of 313.15 K as listed in Table 6- 14. It presents the selectivity and capacity values for the limonene and other ILs. The selectivity for the limonene was found to lower when compared with other ILs. This is a clear indication that limonene performs poorly as a solvent for the separation of n-octane (*i*) and thiophene (*j*). More solvent would be required for the separation of this mixture.

Table 6- 14: A comparison of the selectivity and capacity of solvents for n-octane (*i*) and thiophene (*j*) separation mixture at the temperature of 313.15 K

[1]This work; [2](Nkosi et al., 2018b); [3](Nkosi et al., 2019); [4](He et al., 2020)

	Selectivity ($S_{ij,s}^{\infty}$)	**Capacity ($K_{j,s}^{\infty}$)**
Solvent	**n-octane (*i*)/ethyl acetate (*j*)**	**ethyl acetate (*j*)**
Limonene, [1]	2.73	0.011
DES 2; [4C$_1$NCl] + [Gly] [1:2],[2]	39.12	0.185
DES 3; [4C$_1$NCl] + [Hdiol] [1:1],[3]	109.00	0.924
[PMMIM][NTf$_2$][4]	35.25	0.800

n- heptane (i) and pyridine (j) separation problem

The selectivity and capacity of the limonene for the n-heptane (*i*) and pyridine (*j*) separation problem was compared with ILs at the temperature of 313.15 K as listed in Table 6- 15. The values for the selectivity and capacity listed in Table 6- 15 for the limonene and other ILs show that limonene performs poorly as a solvent due to its low values. However, with the selectivity of greater than one, it still has the potential to separate nitrogen from the mixture of n-heptane (*i*) and pyridine (*j*). Operating costs for such separation would be high, due to the large quantities of solvent required for the desired separation.

Table 6- 15: A comparison of the selectivity and capacity of solvents for n-heptane (*i*) and pyridine (*j*) separation mixture at the temperature of 313.15 K

[1] This work; [2](Nkosi et al., 2018a); [3](Nkosi et al., 2018b)

	Selectivity ($S_{ij,s}^{\infty}$)	**Capacity ($K_{j,s}^{\infty}$)**
Solvent	**n-heptane(*i*)/ pyridine (*j*)**	**pyridine (*j*)**
Limonene, [1]	1.65	0.010
DES 1; (C$_4$H$_{12}$NCl) :(EG) [1:2],[2]	3762.73	2.404
DES 2; [4C$_1$NCl] + [Gly] [1:2],[3]	354.11	1.618

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

In this study, the activity coefficients at infinite dilution of all solutes in limonene solvent were measured by GLC at the temperatures between (303.15 and 333.15) K. It was noted that for all solutes the activity coefficient at infinite dilution decreased with the increase of temperature and increased with the increase of alkyl chain length. The thermodynamic parameters such as enthalpy, entropy and Gibbs free energy at infinite dilution are calculated at the T_{ref} = 313.15 K and these parameters were used to describe the molecular interaction between the solutes and the investigated limonene solvent. It was observed that the triple bond alkyl solutes had a strong interaction with the limonene, due to their low values of activity coefficients at infinite dilution. The partial activity coefficient values for the same solute describe the molecular interaction pattern between the solutes and limonene solvent. The investigated limonene solvents reveal lower values of selectivity and capacity at infinite dilution for the separation mixtures when compared with other ILs. For the fact that the values of selectivity are greater than one, it symbolizes that the limonene solvent can be used for extraction but differ in terms of performances for separating mixtures.

The selectivity and capacity for the separation of hexane/hex-1-ene and ethanol/water showing promising results when compared with other ILs. The selectivity and capacity for the separation mixture heptane/benzene, octane/ethylactetate, heptane/pyridine, octane/pyridine, and octane/thiophene indicates that the limonene is not suitable as the extraction solvent when compared with other ILs.

The separation mixtures of hexane/hex-1-ene and ethanol/water have shown that limonene can be used as an alternative solvent to traditional solvents based on its high selectivity. For future work, more investigation of limonene must be conducted through measurements of liquid-liquid equilibrium and vapour-liquid equilibrium. Such data would provide useful information and understanding into the separation of hexane/hex-1-ene and ethanol/water mixtures.

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APPENDIX A: SUPPLIERS, PURITY AND PROPERTIES OF CHEMICALS

Table A- 1: Suppliers, purity and properties of chemicals.

Compound	Supplier	Chemical Formula	Purity (Mass fraction)	CAS No.
n-pentane	Merck	C_5H_{12}	≥ 99.0	109-66-0
n-hexane	Merck	C_6H_{14}	≥ 99.0	110-54-3
n-heptane	Sigma-Aldrich	C_7H_{16}	≥ 99.0	142-82-5
n-octane	Fluka	C_8H_{18}	≥ 99.9	111-65-9
n-nonane	Merck	C_9H_{20}	≥ 99.0	111-84-2
hex-1-ene	Sigma-Aldrich	C_6H_{12}	≥ 98.0	592-41-6
hept-1-ene	Flucka	C_7H_{14}	≥ 98.0	592-76-7
oct-1-ene	Flucka	C_8H_{16}	≥ 99.5	111-66-0
non-1-ene	Flucka	C_9H_{18}	≥ 95.0	124-11-8
dec-1-ene	Capital lab	$C_{10}H_{20}$	≥ 98.0	872-05-9
hex-1-yne	Sigma-Aldrich	C_6H_{10}	≥ 97.0	628-21-7
hept-1-yne	Fluka	C_7H_{12}	≥ 98.0	628-71-7
oct-1-yne	Fluka	C_8H_{14}	≥ 98.0	629-05-0
cyclopentane	Fluka	C_5H_{10}	≥ 98.5	287-92-3
cyclohexane	ACE	C_6H_{12}	≥ 99.0	11-82-7
cycloheptane	ACE	C_7H_{14}	≥ 99.9	291-64-5
cyclooctane	Sigma-Aldrich	C_8H_{16}	≥ 995	292-64-8
ethanol	Sigma-Aldrich	C_2H_6O	≥ 99.9	64-17-5
methanol	Macron	CH_4O	≥ 99.9	67-59-1
propan-1-ol	Lab scan	C_3H_8O	≥ 99.5	71-23-8
propan-2-ol	Lab scan	C_3H_8O	≥ 99.5	67-63-0
butan-1-ol	Sigma-Aldrich	$C_4H_{10}O$	≥ 99.0	71-36-3
pentan-1-ol	Sigma-Aldrich	$C_5H_{12}O$	≥ 99.0	71-41-0
tert-butanol	Sigma-Aldrich	$C_4H_{10}O$	≥ 99.0	75-65-0
benzene	Sigma-Aldrich	C_6H_6	≥ 99.9	71-43-2
toluene	Sigma-Aldrich	C_7H_8	≥ 99.9	108-88-3
ethylbenzene	ACE	C_8H_{10}	≥ 99.9	100-41-4
acetone	Sigma-Aldrich	C_3H_6O	≥ 99.9	37-64-4
butan-2-one	Sigma-Aldrich	C_4H_8O	≥ 99.7	78-93-3
pentan-2-one	Sigma-Aldrich	C_3H_8O	≥ 99.0	107-87-9
methylacetate	Capital lab	$C_3H_6O_2$	≥ 98.0	79-20-9
ethylacetate	ACE	$C_4H_8O_2$	≥ 99.5	141-78-6
acetonitrile	Sigma-Aldrich	C_2H_3N	≥ 99.7	75-05-08
water	Lab purified	H_2O	≥ 99.9	7732-18-5
thiophene	Sigma-Aldrich	C_4H_4S	≥ 99.9	110-02-1
pyridine	Sigma-Aldrich	C_5H_5N	≥ 99.9	100-86-1
m-xylene	Sigma-Aldrich	C_8H_{10}	≥ 99.9	108-38-3
Helium	Afrox-SA	He	≥ 99.0	7440-49-7
Limonene	Sigma-Aldrich	$C_{10}H_{16}$	≥ 97.0	5989-27-5
dichloromethane	Sigma-Aldrich	$C_6H_4Cl_2$	≥ 99.9	75-09-2

Table A- 2: Antoine Equation Constants for solutes.

Compound	A	B	C	State
n-pentane	7.009	1134.149	238.678	L
n-hexane	6.990	1216.915	227.451	L
n-heptane	7.047	1341.889	223.733	L
n-octane	7.145	1498.959	225.874	L
n-nonane	7.189	1607.736	222.414	L
hex-1-ene	7.056	1266.981	239.628	L
hept-1-ene	7.090	1371.220	232.136	L
oct-1-ene	7.078	1455.841	225.041	L
non-1-ene	7.148	1551.558	217.790	L
dec-1-ene	7.315	1694.625	215.316	L
hex-1-yne	7.220	1336.557	236.713	L
hept-1-yne	7.090	1371.220	232.136	L
oct-1-yne	6.933	1357.835	208.910	L
cyclopentane	7.043	1202.530	239.690	L
cyclohexane	6.889	1200.826	218.815	L
cycloheptane	7.011	1417.934	224.495	L
cyclooctane	7.207	1570.930	217.914	L
ethanol	8.129	1660.871	238.131	L
methanol	8.084	1580.459	239.096	L
propan-1-ol	7.777	1518.796	213.076	L
propan-2-ol	7.825	1482.133	217.413	L
butan-1-ol	7.301	1285.023	173.247	L
pentan-1-ol	7.215	1333.460	169.781	L
tert-butanol	7.138	1069.762	168.931	L
benzene	6.814	1090.431	197.146	L
toluene	7.137	1457.287	231.827	L
ethylbenzene	7.156	1559.545	228.582	L
acetone	7.317	1315.674	240.479	L
butan-2-one	7.191	1323.071	227.093	L
pentan-2-one	7.374	1553.014	243.751	L
methylacetate	7.285	1277.214	233.155	L
ethylacetate	7.2601	1338.5652	228.608	L
acetonitrile	7.544	1583.400	257.887	L
water	8.108	1750.286	235.000	L
thiophene	7.070	1296.880	225.437	L
pyridine	7.184	1462.741	224.598	L
m-xylene	7.181	1573.024	226.671	L

Table A- 3: Physical and Critical Properties, Critical Temperature, T_c critical pressure, P_c critical volume, V_c acentric factor, ω ionization energy, I_c of the solute and the helium gas used in the calculation for virial coefficients.

Compound	T_c (K)	P_c (Bar)	V_c /cm^3.mol^{-1}	ω	I_c /kJ.mol^{-1}
n-pentane	469.7	33.7	311	0.252	998.6
n-hexane	507.5	30.1	370	0.299	977.4
n-heptane	540.2	27.4	428	0.35	957.1
n-octane	568.7	24.9	492	0.399	947.5
n-nonane	594.6	22.9	555	0.445	937.8
hex-1-ene	504	31.43	355.1	0.281	910.8
hept-1-ene	537.1	29.2	409	0.358	910.8
oct-1-ene	566.7	26.2	464	0.386	910.0
non-1-ene	592	23.4	580	0.43	909.0
dec-1-ene	616.4	21.1	584	0.478	908.9
hex-1-yne	539.3	331	376.2	0.146	960.0
hept-1-yne	537.3	28.3	440	0.358	960.0
oct-1-yne	598.5	31.01	441	0.262	960.0
cyclopentane	512.6	80.97	118	0.224	1046.9
cyclohexane	553.8	40.7	308	0.212	951.3
cycloheptane	604.2	38.2	353	0.237	962.0
cyclooctane	647.2	35.6	410	0.236	941.7
ethanol	513.9	61.48	167	0.649	1010.2
methanol	512.6	80.97	118	0.565	1046.9
propan-1-ol	536.8	51.75	219	0.629	982.2
propan-2-ol	508.3	47.62	220	0.665	981.3
butan-1-ol	563.05	44.23	275	0.59	964.8
pentan-1-ol	586.15	38.7	327	0.592	964.9
tert-butanol	506.21	39.9	276	0.613	935.9
benzene	562.2	48.95	256	0.212	892.2
toluene	591.8	41.08	316	0.263	851.0
ethylbenzene	617.2	36.09	374	0.304	846.2
acetone	508.1	47	209	0.307	935.9
butan-2-one	536.8	24.1	267	0.322	918.5
pentan-2-one	561.08	37.1	301	0.345	895.4
methylacetate	506.8	46.9	228	0.326	989.0
ethylacetate	523.2	38.3	286	0.362	966.0
acetonitrile	545.0	48.3	173	0.327	1177.3
water	647.3	221.2	57.1	0.344	951.3
thiophene	579.4	56.9	219	0.196	855.0
pyridine	620.0	56.3	254	0.243	892.5
m-xylene	617.1	35.4	376	0.259	825.9

Physical properties of limonene

Table A- 4: Density and refractive index at temperature of (293.15-333.15) K for the limonene.

Temperature (K)	Exp density (ρ) g/cm^3	Exp refractive index (*n*)
293.15	0.8444	1.4728
298.15	0.8405	1.4705
303.15	0.8366	1.4681
308.15	0.8327	1.4656
313.15	0.8287	1.4632
318.15	0.8248	1.4608
323.15	0.8209	1.4583
328.15	0.8169	1.4559
333.15	0.8129	1.4535

[b](SigmaAldrich, 2020)

Table A- 5: Viscosity and speed of sound at temperature of (293.15-313.15) K for the limonene.

Temperature (K)	Exp viscosity (μ) mPa.s	Exp speed of sound (s) m.s^{-1}
293.15	0.9870	1340.16
298.15	0.9110	1320.81
303.15	0.8560	1301.21
308.15	0.800	128173
313.15	0.7530	1256.76

APPENDIX B: SAMPLE CALCULATION

The sample calculation of calculating the infinite dilution activity coefficient for pentane using 33 % solvent loading, at *T*= 313.15 K

$$J_2^3 = \left(\frac{2}{3}\right)\left[\frac{\left(\frac{P_i}{P_o}\right)^3 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1}\right] \tag{B- 1}$$

$$J_2^3 = \left(\frac{2}{3}\right)\left[\frac{\left(\frac{113400}{100900}\right)^3 - 1}{\left(\frac{113400}{100900}\right)^3 - 1}\right]$$

$$J_2^3 = 1.0631$$

$$U_o = U\left[1 - \frac{P_w^o}{P_o}\right]\frac{T}{T_f} \tag{B- 2}$$

$$U_o = 3.4435 \times 10^{-7}\left[1 - \frac{2576.8014}{100900}\right]\frac{313.15}{296.45}$$

$$U_o = 3.5446 \times 10^{-7} m^3 . s^{-1}$$

Net retention volume

$$V_N = (J_2^3)^{-1} U_o (t_r - t_G)\frac{T_{col}}{T_f}\left[1 - \frac{P_w^o}{P_o}\right] \tag{B- 3}$$

$$V_N = (\ 1.0631)^{-1}(53.88 - 40.74)\ \times 3.5446 \times 10^{-7}$$

$$V_N = 4.3810\ \times 10^{-6}$$

Second virial coefficient of the solute

$$B/_{V_c} = 0.43 - 0.886\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375\ (n-1)\ \left(\frac{T_c}{T}\right)^{4.5} \qquad \text{(B- 4)}$$

$$B_{11} = 0.43 - 0.886\left(\frac{238.678}{313.15}\right) - 0.694\left(\frac{238.678}{313.15}\right)^2 - 0.0375\ (5-1)\ \left(\frac{238.678}{313.15}\right)^{4.5}$$

$$B_1 = -0.0011\, m^3.mol^{-1}$$

Solute molar volume

$$V^* = V_C(0.29056 - 0.08775\omega)\ e^{\left[1-\frac{T}{T_C}\right]^{\frac{2}{7}}} \qquad \text{(B- 5)}$$

$$V^* = 311 \times 1 \times 10^{-6}\ (0.29056 - 0.08775\ \times 0.252)\ e^{\left[1-\frac{313.15}{469.7}\right]^{\frac{2}{7}}}$$

$$V^* = 0.00012$$

Mixed Critical properties

$$I_{C12} = (I_{C11} + I_{C22})^{1/2} \left(V_{C11}^{1/3} + V_{C12}^{1/3}\right)^6 \tag{B- 6}$$

$$I_{C12} = (998.6 + 2372.56)^{1/2} \times 10^3 \left[(311 \times 10^{-6})^{\frac{1}{3}} + (57.4 \times 10^{-6})^{\frac{1}{3}}\right]^6$$

$$I_{C12} = 4.8711\, J.mol^{-1}$$

$$V_{C12} = \frac{1}{8} \left(V_{C11}^{1/3} + V_{C12}^{1/3}\right)^3 \tag{B- 7}$$

$$V_{C12} = \frac{1}{8} \left[(311 \times 10^{-6})^{\frac{1}{3}} + (57.4 \times 10^{-6})^{\frac{1}{3}}\right]^3$$

$$V_{C12} = 0.0002\, m^3$$

$$T_C = 128\, (T_{C11}.T_{C22})^{1/2}\, (I_{C11}.I_{C22})^{1/2} \left({}^{V_{C11}.V_{C22}}\!/_{I_{C12}}\right) \tag{B- 8}$$

$$T_C = 128\, (5.5 \times 469.7)^{1/2}\, (2372.57 \times 998.6 \times 10^3)^{1/2} \left(\frac{311 \times 57.4 \times 10^{-6}}{4.8711}\right)$$

$$T_C = 36.6986\, K$$

Cross second virial coefficient of the solute and carrier gas

$$B/_{V_c} = 0.43 - 0.886\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375\,(n-1)\,\left(\frac{T_c}{T}\right)^{4.5} \qquad \text{(B- 9)}$$

$$B/_{V_c} = 0.43 - 0.886\left(\frac{36.6986}{313.15}\right) - 0.694\left(\frac{36.6986}{313.15}\right)^2$$

$$- 0.0375\,(3-1)\,\left(\frac{36.6986}{313.15}\right)^{4.5} \times 0.0002$$

$$B_{12} = 0.000048\, m^3.mol^{-1}$$

Infinite dilution activity coefficient

The equation for calculating the IDAC was broken down into three terms:

$$\ln\gamma_{13}^{\infty} = \left(\frac{n_3\, RT}{V_N P_i^o}\right) - \frac{(B_{11} - v_1^*)P_i^o}{RT} + \frac{(2B_{12} - v_1^{\infty})J_2^3 P_o}{RT} \qquad \text{(B- 10)}$$

Term 1:

$$\ln\gamma_{13}^{\infty} = \ln\left(\frac{n_3\, RT}{V_N P_i^o}\right)$$

$$\ln\gamma_{13}^{\infty} = \ln\left(\frac{0.0049 \times 8.314 \times 313.15}{4.3810\ \times 10^{-6} \times 114382.5994}\right)$$

$$\gamma_{13}^{\infty} = 25.6609$$

Term 2:

$$\ln\gamma_{13}^{\infty} = \frac{(B_{11} - v_1^*)P_i^o}{RT}$$

$$\ln\gamma_{13}^{\infty} = \frac{(-0.0011 - 0.00012) \times 114382.5994}{8.314 \times 313.15}$$

$$\gamma_{13}^{\infty} = 1.0529$$

Term 3:

$$\ln\gamma_{13}^{\infty} = \frac{(2B_{12} - v_1^{\infty})J_2^3 P_o}{RT}$$

$$\ln\gamma_{13}^{\infty} = \frac{(2 \times 0.000048 - 0.00012)1.0631 \times 114382.5994}{8.314 \times 313.15}$$

$$\gamma_{13}^{\infty} = 0.9989$$

$$\gamma_{13}^{\infty} = Term\ 1 + Term\ 2 + Term 3$$

$$\gamma_{13}^{\infty} = 25.6609 + 1.0529 + 0.9989$$

$$\gamma_{13}^{\infty} = 26.9883$$

Estimation of the experimental uncertainty

In this study, the estimation of the combined uncertainty for the infinite dilution activity coefficient can be obtained by adding the square of the uncertainties due to the repeatability and experimental measurements. The combined uncertainty was calculated using Equation (B-11).

$$u(\gamma_{13}^{\infty}) = \sqrt{\left[u_{rep}(\gamma_{13}^{\infty})\right]^2 + [u_{eve}(\gamma_{13}^{\infty})]^2} \qquad \text{(B- 11)}$$

The highest number of the uncertainty for the infinite dilution activity coefficient on this study was found to be 24.69%.

Table B- 1: Combined uncertainty on experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene at temperature of (303.15 – 333.15) K.

	Experimental uncertainty at T/K			
Solutes (i)	T=303.15	T=313.15	T=323.15	T=333.15
n-Pentane	8.686	5.700	2.564	3.585
n-Hexane	10.282	10.993	7.305	4.738
n-Heptane	18.363	6.862	2.513	1.044
n-Octane	29.289	19.761	7.104	1.467
n-Nonane	41.403	32.274	23.679	14.266
Hex-1-ene	3.802	1.005	0.156	0.404
Hept-1-ene	11.174	6.302	2.523	0.453
Oct-1-ene	21.762	12.702	12.162	8.794
Non-1-ene	36.310	18.288	15.968	9.894
Dec-1-ene	39.668	1.286	4.456	16.763
Hex-1-yne	9.263	4.780	1.446	2.300
Hept-1-yne	0.473	1.570	1.704	9.373
Oct-1-yne	12.768	7.126	4.500	0.093
Cyclopentane	3.035	3.910	2.841	2.638
Cyclohexane	6.274	5.862	4.713	1.268
Cycloheptane	12.080	11.275	7.682	6.970
Cyclooctane	19.544	16.967	13.293	10.013
Thiophene	3.993	0.266	1.630	4.030
Pyridine	21.514	16.937	12.117	8.514
Ethanol	29.358	16.402	7.878	5.587
Methanol	16.637	10.502	7.079	3.193
Propan-1-ol	39.940	28.843	18.659	14.388
Propan-2-ol	30.624	19.419	11.991	6.290
Butan-1-ol	48.157	27.931	23.171	20.527
Pentan-1-ol	40.550	35.767	30.599	28.205
tert-Butanol	21.422	13.575	9.083	5.019
Benzene	3.304	2.481	0.061	0.277
Toluene	3.295	3.642	1.990	1.599
Ethylbenzene	1.088	2.614	2.016	1.225
m-Xylene	1.950	1.245	0.684	3.452
Acetone	5.070	1.155	1.001	1.558
Butan-2-one	8.542	3.155	0.858	0.446
Pentan-2-one	14.124	8.898	5.487	3.589
Methylacetate	0.211	1.758	2.522	2.700
Ethylacetate	3.061	0.566	2.281	3.922
Acetonitrile	4.634	0.066	0.551	1.982
Water	5.430	1.887	2.236	1.434

Table B- 2: Combined uncertainty (in percentages) on experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene at temperature of (303.15 – 333.15) K.

	Experimental uncertainty at T/K			
Solutes (i)	T=303.15	T=313.15	T=323.15	T=333.15
n-Pentane	20.46	18.31	11.67	20.01
n-Hexane	9.84	14.03	12.06	10.23
n-Heptane	8.75	4.12	1.92	1.05
n-Octane	9.94	7.95	3.58	0.92
n-Nonane	12.47	10.32	8.54	6.20
Hex-1-ene	3.81	1.32	0.28	0.95
Hept-1-ene	6.46	4.64	2.38	0.56
Oct-1-ene	8.68	6.23	7.32	6.58
Non-1-ene	12.09	6.88	6.93	5.12
Dec-1-ene	11.88	0.45	1.58	6.43
Hex-1-yne	8.95	5.94	2.27	4.47
Hept-1-yne	0.34	1.37	1.76	11.43
Oct-1-yne	6.55	4.15	3.01	0.07
Cyclopentane	4.33	7.13	6.67	7.76
Cyclohexane	4.41	5.22	5.48	1.86
Cycloheptane	5.68	6.13	5.15	5.66
Cyclooctane	7.74	7.31	6.56	5.83
Thiophene	3.68	0.29	2.21	6.64
Pyridine	24.69	21.53	17.65	13.65
Ethanol	15.93	11.14	6.71	5.89
Methanol	12.28	10.15	8.88	5.13
Propan-1-ol	19.47	16.17	12.18	11.04
Propan-2-ol	15.19	11.87	9.03	5.84
Butan-1-ol	20.48	13.43	13.01	13.41
Pentan-1-ol	19.20	18.16	16.34	15.97
tert-Butanol	10.06	8.09	7.06	5.01
Benzene	2.56	2.34	0.07	0.42
Toluene	2.24	2.76	1.74	1.62
Ethylbenzene	0.63	1.57	1.33	0.91
m-Xylene	1.08	0.75	0.45	2.60
Acetone	5.39	1.59	1.72	3.31
Butan-2-one	6.58	3.00	1.02	0.64
Pentan-2-one	9.47	6.92	5.05	3.91
Methylacetate	0.25	2.84	5.32	7.05
Ethylacetate	2.74	0.62	3.25	6.81
Acetonitrile	2.36	0.04	0.49	2.20
Water	10.35	4.50	6.80	5.57

APPENDIX C: JOURNAL ABSTRACT

Assessment of Limonene as green solvent for separation processes

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Abstract - The infinite dilution activity coefficients for various solutes, which include alkanes, alkenes, alkynes, cycloalkanes, heterocycles, alcohol, aromatics, ketones, ethers, nitrile and water in the limonene solvent were measured by gas-liquid chromatography at four different temperatures, namely 303.15 K, 313.15 K, 323.15 K and 333.15 K. In this study, limonene which is a non-polar solvent extracted from essential oils of the citrus peels employing distillation was investigated as an alternative solvent to currently employed conventional organic solvents in separation processes. Through the experimental infinite dilution activity coefficients γ_{13}^{∞}, values of partial molar excess enthalpy at infinite ($\Delta H_i^{E,\infty}$) were obtained using the Gibbs-Helmholtz equation. In addition, infinite dilution selectivity (S_{ij}^{∞}) and capacity (Δk_j^{∞}) values were calculated from the experimental limiting activity coefficients and were compared with ionic solvents. From the study, it was observed that limonene can be used as an alternative for separation processes. Activity coefficients at infinite dilution of different organic solutes in hexadecane were measured at various temperatures to validate the reliability and accuracy of gas-liquid chromatography.

Keywords - Gas liquid chromatography, infinite dilution activity coefficient, limonene, separation.