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EXPERIMENTAL MEASUREMENT OF SORET COEFFICIENT OF BINARY HYDROCARBON MIXTURES

By

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A dissertation presented to

Ryerson University

in partial fulfillment of the

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DOCTOR OF PHILOSOPHY

in the Program of

MECHANICAL & INDUSTRIAL ENGINEERING

Toronto, Ontario, Canada, 2013

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Abstract

Experimental Measurement of Soret Coefficient of Binary Hydrocarbon Mixtures

Doctor of Philosophy

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Mechanical & Industrial Engineering

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Measurement of diffusion coefficients is essential for simulation and prediction of oil reservoirs. Recently, a new experimental set-up has been built at Ryerson University to measure the transport coefficient of transparent liquid mixtures. Laser-based optical digital interferometry techniques using a Mach-Zehnder Interferometer have been used for measuring the diffusion coefficients. This method is non-intrusive, highly accurate, and can provide a detailed 2-D visualization of temperature and concentration fields. Five binary liquid mixtures of Decane (C₁₀H₂₂) - Isobutylbenzene (IBB), Decane (C₁₀H₂₂) - 1,2,3,4 Tetrahydronaphthalene (THN), Dodecane ($C_{12}H_{26}$) - Isobutylbenzene (IBB), Dodecane ($C_{12}H_{26}$) - 1,2,3,4 Tetrahydronaphthalene (THN) and Isobutylbenzene (IBB) - 1,2,3,4 Tetrahydronaphtha-lene (THN) have been selected. The mixtures have been prepared from pure $C_{10}H_{22}$, $C_{12}H_{26}$, IBB and THN for 50% mass fractions. These five binary mixtures are representatives of binary interactions between alkane, one-ring aromatic and two-ring aromatic hydrocarbons. The thermal designs of the diffusion cell, as well as the data analyze method, have been improved. A comparison of experimental data with theoretical analysis based on the Firoozabadi model for measuring thermodiffusion coefficient and Peng-Robinson equation of state (PR-EOS) for measuring the physical properties

have been conducted. Experimental results showed a maximum deviation of less than 2% for IBB- $C_{12}H_{26}$ and THN-IBB and 9% for THN- $C_{12}H_{26}$ from the available benchmark results.

Accurate knowledge of refractive index is highly relevant to correlations with concentration, temperature, wavelength and pressure in non-intrusive experiments carried out with transparent fluids. It can be used for the identification and characterization of pure materials and for the measurement of concentration of multi-component mixtures. In this current scope, refractive indices of five binary mixtures $C_{10}H_{22}$ -IBB, $C_{10}H_{22}$ -THN, $C_{12}H_{26}$ -IBB, $C_{12}H_{26}$ -THN and IBB-THN have been measured using both the Mach-Zehnder Interferometer and a multi-wavelength Abbemat refractometer. Temperature and concentration coefficients of refractive indices, or so-called contrast factors, as well as their individual correlation to calculate refractive indices have been presented for a wide range of visible spectrums such as 436 nm to 657 nm. Comparison with available literature and mixing rules shows that new correlations can predict the experimental data with deviations of less than 0.001.

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Nomenclature

С	Mass	fraction	of the	liquid	(-))
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- D_M Solutal diffusion coefficient (m².s⁻¹)
- D_T Thermal diffusion coefficient (m².s⁻¹.K⁻¹)
- f_i Fugacity of component *i* (-)
- *h* Height of the cavity (m)
- k_f Conductivity of the fluid (W.m⁻¹.K⁻¹)
- *p* Pressure (Pa)

$$S_T$$
 Soret coefficient = $\frac{D_T}{D_M}$ (K⁻¹)

- t Time (s)
- T Temperature (°C or °K)
- Δc Concentration difference (-)
- ΔT Temperature difference = $T_H T_C$ (K)

Greek Symbols

- α Thermal diffusivity (m².s⁻¹)
- α_T Thermal diffusion factor T.S_T. α (-)
- β_T Thermal volume expansion (K⁻¹)
- μ Dynamic viscosity (kg.m⁻¹.s⁻¹)
- *v* Kinematic viscosity $(m^2.s^{-1})$
- ρ_o Density of the fluid at reference temperature T_o (kg.m⁻³)

Chapter 1

Introductions and Motivation

1.1 Introduction

In a closed system, the concentration gradients build up due to the applied temperature gradient until the system reaches a steady state condition. Such a phenomenon is called the Soret effect, Ludwig-Soret effect, thermodiffusion, or thermal diffusion [1]. This phenomenon was named after Swiss physicist and chemist Charles Soret [2], who studied it in detail. Though, Soret was not the first person to notice this phenomenon. In 1856, before Soret's discovery of thermodiffusion effect, German physician Carl Friedrich Wilhelm Ludwig [3] noticed that solute concentrated near the cold wall of a U-tube. The thermodiffusion effect has been measured with a parameter called Soret coefficient. Numeric values of it in liquids are very small, usually orders of 10⁻³ K⁻¹ only, and therefore, the Soret effect remains small in liquid mixtures. Although in early years thermodiffusion was studied mainly in gases and aqueous mixtures, one of the most important and practical applications of thermodiffusion is the distribution of components in a natural hydrocarbon reservoirs [4]. As shown in figure 1.1, in a hydrocarbon reservoir, both temperature and pressure of the fluids are very close to the critical region [5]. Therefore, the distribution of component is very sensitive to natural forces such as gravity, pressure, and geothermal gradients. These forces create the compositional variations induced by phase separation and diffusion.



Figure 1.1 Importance of measuring Soret coefficients of modelling hydrocarbon reservoir If we consider the linear laws of irreversible thermodynamics and neglect the pressure gradient, the mass flux of *i*th component in a mixture of *P* components can be written as [1],

$$\vec{J}_{i} = -\rho_{o} \sum_{k=1}^{P-1} D_{ik} \vec{\nabla} c_{k} - \rho_{o} D_{Ti} c_{io} (1 - c_{io}) \vec{\nabla} T$$
(1.1)

Where, ρ_o is the specific mass or density, c_i is the mass fraction of the reference component with initial value equal to c_{io} , D_{ik} is the isothermal molecular diffusion coefficient, D_{Ti} is the thermodiffusion coefficient and $\vec{\nabla}c_i$ is the gradient of mass fraction induced by temperature gradient of $\vec{\nabla}T$. For the binary mixtures, the mass diffusion flux \vec{J}_1 of component 1 induced by temperature (*T*) and mass fraction (c_1) gradient can be written as [6; 7],

$$\vec{J}_{1} = -\rho_{o} D_{M} \vec{\nabla} c_{1} - \rho_{o} D_{T} c_{1o} (1 - c_{1o}) \vec{\nabla} T$$
(1.2)

The first term in the right side of equation (1.1) and (1.2) is Fick's law [8; 9] of diffusion which describes homogenization by normal diffusion and the second term is the Soret effect or thermodiffusion effect which describes mass separation due to a temperature gradient. The two terms are of opposite sign and of equal intensity. On the conditions with net mass flux i.e. $\vec{J}_1 = 0$,

$$\vec{\nabla}c_1 = -\frac{D_T}{D_M}c_{1o}(1 - c_{1o})\vec{\nabla}T$$
(1.3)

The ratio $\frac{D_T}{D_M}$ is called the Soret coefficient S_T of component 1 and can be written from equation

(1.3) as,

$$S_T = \frac{-1}{c_{1o}(1 - c_{1o})} \frac{\nabla c_1}{\nabla T}$$
(1.4)

Here, an important point to be noted that $S_{\rm T}$ of second component can also be expressed using equation (1.4), by using the concentration of (1- c_1) as reference component. So, the numerical value of the Soret coefficient of the second component is the same, but opposite in sign, which is $-S_{\rm T}$. The molecular diffusion coefficient is always positive. However, the Soret coefficient can be positive or negative or even zero [10; 11; 12], depending on the sign and value of $D_{\rm T}$ or on the sense of migration of the reference component towards the cold or hot wall. If the fluid is incompressible, variations of temperature and concentration are small, and the coefficients $D_{\rm M}$, $D_{\rm T}$ and $S_{\rm T}$ can be treated as the averaged constant coefficients of mean temperature T_o and mean concentration c_{1o} .

1.2 Objectives

The three main objectives of this research are: (a) to provide correlations for measuring refractive indices as a function of concentration, temperature, and wavelength of 436 nm to 657 nm. These correlations can be used to calculate refractive indices at known concentration,

temperature and wavelength; (b) to build a laser-based experimental set up for measuring coefficients of refractive indices and Soret coefficients of binary mixtures. Laser based optical system is nonintrusive and provide detail 2-D information; and (c) measurement of Soret coefficients and comparison with the available theoretical approach.

1.3 Thesis organization

This thesis consists of following seven chapters: (a) chapter 1 presents introduction; (b) chapter 2 presents brief concepts of Soret effect and historical literature review of experimental and theoretical works; (c) chapter 3 presents fluid material and details experimental methodologies; (d) chapter 4 presents the measurement of refractive indices and coefficients of refractive indices; (e) chapter 5 presents measurement of Soret coefficients; (f) chapter 6 presents a detailed error analysis; and (g) finally chapter 7 represents conclusions, contribution and future works.

Chapter 2

Historical review of thermodiffusion coefficients

2.1 Review of experimental attempts

As already mentioned in previous chapter, Soret effect is named after Swiss physicist and chemist Charles Soret (September 23, 1854 to April 4, 1904). However, Soret is not the first person to be noticed this phenomenon in liquid system. In 1856, German physician Carl Friedrich Wilhelm Ludwig (December 29, 1816 to April 23, 1895) [3] filled 8.98% Sodium sulphate solution in a rubber U-tube, maintained two ends of the tube in ice water and boiling water respectively. He noticed that solute concentrated near the cold wall of the U-tube. Charles Soret kept sodium chloride and potassium nitrate in a vertical tube of 30 cm length and 2 cm diameter, maintained top and bottom end of the tube at 80 °C and room temperature respectively and noticed that concentration of salt solutions in a tube does not remain uniform. One very interesting thing has been found in the published biographies about Ludwig's life and carrier, most of the writers [13; 14] of his biographies highlighted his tireless research works in physiology or medical science. However, they overlooked Ludwig's contribution on thermodiffusion.

From 1879 to 1884, Soret published several papers original texts in French based on his thermodiffusion experiments which have been summarized and briefly discussed in English by Platten and Costesèque [2]. Same thermodiffusion phenomenon of suspended particles in carrier liquid or gas is called thermophoresis [15]. Irish physicist John Tyndall [16] became the first to observe that temperature gradient affects dust particle's motion in gas mixtures. Without detail scientific discussion, he simply reported it in his Royal Institute lecture titled as 'On Haze and Dust' and included it in his book 'Scientific Addresses' published in 1870. Later on, Chapman [17] studied thermodiffusion in gases experimentally and provided kinetic theory for monatomic gases in 1916.







(c) John Tyndall in 1850

(a) Carl Ludwig in 1859

(b) Charles Soret

Figure 2.1 Photographs of C. Ludwig, C. Soret and J. Tyndall

Though thermodiffusion has been discovered more than 150 years ago, accurate data of thermodiffusion measurements are scarcely available in literature for the liquids. Several numerical or theoretical approaches exist in literature [18] for predicting thermodiffusion coefficients in liquid and gas mixtures. However, the predictions of those models are different and contradictory. As experimental data are more reliable, scientists need to have experimental data from good experimental techniques to improve the theoretical models.

2.1.1 Early attempts

Naturally, the gravitational force is always present in terrestrial conditions and it affects thermodiffusion experiments by mixing the system. So, instead of avoiding gravitational effect, scientists have tried to take the advantages of it by coupling gravity in to thermodiffusion process. Thermodiffusion column or thermogravitational column or Clusius-Dickel column is widely used in industry for purification of gas mixtures. In 1938, Clusius and Dickel [19] showed that when gas is placed in between two concentric cylinders, where inner cylinder is heated and outer cylinder is cooled, gas concentration varies between top and bottom of the column. Farber and Libby [20] improved the apparatus in 1940 and studied effects of variation of gravity by rotating the apparatus in different speeds. They showed that gas separation is in maxima when the rotational speed is around 400 rpm, separation decreases drastically for below or higher of this speed.

In early times, thermodiffusion was studied for isotope separation [21; 22], nuclear fusion in ionized gas [23], diffusion in Sun [24] etc. Later on, up to the year of early seventies, Clusius-Dickel column was adopted by other scientists [25; 26; 27; 28; 29] to study thermodiffusion separation in liquid mixtures. In 1956, Danby and his co-workers [30] experimentally showed that separation of binary liquid hydrocarbon is possible using thermogravitational (or Clusius-Dickel) column process. They did experiment in a one meter long Clusius column for binary mixture of n-Pentene with neo-Pentene and found significant increase of concentration of n-Pentene at the bottom of the column.

In 1975, Saviron et al. [31] used the column to measure thermodiffusion of isotope mixtures. In recent years, lot of studies have been done by modifying the actual cylindrical thermogravitational column with a plane-thermogravitational column [32; 33], inclined column [34], packed column to study Soret effect in porous medium [35] etc. This method is equally used for binary [36; 37] and ternary liquid mixtures [38]. Now-a-days, it is widely used as modified form in biology [39] and nuclear energy research [40].

In 1954, Saxton and his co-workers [41] introduced a membrane cell, where the twin cell is separated by a membrane such as porous glass and each cell has independent magnetic stirrer to maintain uniform concentration. They found an optimum porous size to have no convection in the system. In both top and bottom heating condition, their results remain unchanged. Later on, Rassoul and Bott [42] used similar cell, where cell membrane was made from 2 to 10 micron size of metal disk. They did not use stirrer and did not provide any figure of their results. However, they mentioned that some of their result for n-heptane-benzene mixture was consistent with the work of Bierlein [43] and for benzene-carbon tetrachloride mixture was consistent with Guczi and Tyrrell [44].

From 1966 to 1969, Turner and his co-workers [45; 46; 47; 48] did a series of thermodiffusion experiments of binary liquids using flow cells. A Flow cell is another type of top heated convectionless horizontal diffusion cell where liquid continuously flows from one side in a laminar motion style through the gap between two parallel plates and collected from other side which has a sharp edged wedge-shaped blade located in the middle of the duct. Wedge-shaped blade helps to separate the liquid equally in to two halves such as top and bottom parts. Liquids have been collected in separate tanks and analyzed to calculate the Soret and diffusion coefficients. The apparatus is simple in design and easy to use, however precise calibration is required. The method of calculating Soret coefficients and phenomenology can be found in literature [49]. Having larger aspect ratio, flow cell is good for measuring Soret coefficient in organic solutions [50].

Rayleigh-Bénard is a less popular experimental method to measure negative Soret coefficient of liquid mixture by heating from the bottom wall [50]. Unlike intentional scientific discoveries, there are plenty of discoveries happened by chance, discovery of Bénard cells is one of those incidents. In 1898, French scientist Henri Bénard discovered polygonal cells named 'cellular vortices', later on renamed as 'Bénard cells'. Bénard continued doing experiments of

one millimeter thin liquid layer of upper surface open to air and bottom surface maintained in constant temperature. While increasing the temperature of the bottom surface slowly, he observed Bénard cells in two steps namely initial phase and second phase for all types of liquids for specific amount of temperatures. He observed rising streams of convective flow in the middle of the cell and descending streams near the boundaries of convective flow inside the cells using Schlieren beam deflection method. However, Bénard did not provide enough theoretical expressions of his excellent experimental work and he did not explaine the role of surface tension of onset of instability.

In 1916, Lord Rayleigh [51] published the necessary critical temperature difference to onset the convective instability. He found that for onset of instability, the wavelength of the convective cells is required to have two times the thickness of the liquid, which was confirmed by Bénard's later works of 1928 and 1938. Later on, it was scientifically proved that the convective instability is caused by the combination of buoyancy and the Marangoni effect. The details descriptions of his observation and his scientific biography can be found in the book [52] of J. E. Wesfried published in 2006. This method is used to calculate Soret coefficient by bottom heating of the Soret cell and measuring critical Rayleigh number and Hopf frequency at the temperature gradient of onset of free convection [6]. The critical Rayleigh number of Rayleigh-Bénard instability for which the convective cells appear is 1708 [53].

In 1974, Giglio and Vendramini [54] became the first to discover thermal lens method of measuring thermodiffusion coefficient in Aniline-Cyclohexane mixture. In this method fluid is heated by the laser itself to create a concave shaped lens in liquid due to the thermal expansion of the liquid. Though relaxation time of this method is very small as compare to classical Soret cell and thermogravitational technique, this method is not very popular due to the high sensitivity to

convection. Recently, Alves and his coworkers [55; 56; 57] modified this method and used for measuring thermodiffusion coefficients of magnetic colloids. In 1975, Giglio and Vendramini [58] used the combination of Soret cell and beam deflection technique for measuring Soret coefficients. For measurement of thermodiffusion coefficient of liquid mixtures in convectionless systems, Soret cell is used for beam deflection technique (BDT). In this technique, the incoming laser beam deflects due to the change of refractive index induced by temperature or concentration gradient. The deflection of beam is recorded by a CCD detector and use to measure change of temperature or concentration. Now-a-days, this method is widely used for binary mixtures using single laser [59; 60] and for ternary mixtures [61] using two lasers of different wavelengths.

In 1978, Thyagarajan and Lallamand [62] showed that thermodiffusion factor ($\alpha_T = S_T.T_0$) of binary mixtures of Carbon disulphide (CS₂)-Ethanol can be determined using another optical method named 'Thermal Diffusion Forced Rayleigh Scattering (TDFRS) or Holographic Grating Technique'. This is another popular technique of simultaneous measurement of three physical properties of liquids such as molecular diffusion coefficient, Soret coefficients and thermal diffusivity.

In this technique, a beam splitter splits a single laser beam into two laser beams of same intensity which are focused on a sample containing the liquid mixture to create interference grating. Small amount of chemically inert dye is added to the liquid to provide self absorption coefficient, which converts light intensity grating in to the temperature grating. This temperature grating automatically causes concentration grating due to the Soret effect. Both temperature and concentration grating combine together and contribute to refractive index grating, which is read by diffraction of a third laser beam. During 1987 to 1988, Bloisi and his coworkers [63; 64] were

inspired by the experimental evidence of Thyagarajan and Lallamand and studied the Soret effect to measure temporal behaviour of the concentration grating of TDFRS and provided explicit expression for the diffracted signal of TDFRS technique as a function of driving parameters and material properties. Recently, comparison showed good agreement between TDFRS method and convective coupling method i.e. thermogravitational cell method by Blanco et al. [65]. Unlike Soret cell, this technique has very short characteristic time i.e. few milliseconds, which is a big advantage of measuring Soret coefficient. However, the experiment has to be repeated many times [6].

In last decade, a modification of TDFRS technique named microfluidic fluorescence is now widely used in biological systems. Braun and his co-workers [66; 67] measured thermodiffusion coefficients of DNA by heating the water using an infrared laser and measuring the change of DNA concentration due to the thermodiffusion from florescent intensity. A combination of thermodiffusion and convection has been studied to produce colloidal crystal [68], which has application both in biological system and rock near hydrothermal vents.

Since the discovery of thermodiffusion by Soret and Ludwig, many scientists have tried to measure Soret coefficients of various liquid and gas mixtures using different techniques and operating conditions. However, scientists were realizing the lack of benchmark data for comparison of different techniques. In 1999, five different research groups agreed to measure the Soret coefficient at mean temperature of 25°C for three binary mixtures of Dodecane ($C_{12}H_{26}$), Isobutylbenzene (IBB) and 1,2,3,4-Tetrahydronaphthalene (THN) which are the representatives of alkenes, one-ring and two-ring components as shown in Figure 2.2. Five groups used four different techniques to measure Soret coefficients, which are: parallelepiped thermogravitational column technique along with open-ended capillary technique [69], TDFRS or holographic grating technique [70; 71], annular thermogravitational column [72] and packed thermogravitational column [35]. Later on, Mialdun and Shevtsova [73] added data of optical digital interferometry technique and Koniger et al. [60] added data of beam deflection technique to the benchmark data.



Figure 2.2 Molecular structures of pure components

2.2.2 Soret cell and interferometry methods in thermodiffusion

In 1927, Tanner [74] studied Soret effect on various liquid mixtures using optical method of a 10 mm height top heated transparent Soret cell. After many years, he tested different cell geometries, improved the design of diffusion cell to calculate both Soret and molecular diffusion coefficient and claimed that Soret coefficient is independent of cell height [75; 76]. From 1951 to 1954, Thomaes and his co-worker [77; 78] used similar diffusion cell and optical method to measure Soret coefficient of various organic compounds. Bierlein and his co-worker [79; 80] provided the allowable temperature difference and thickness of the diffusion cell.

In 1958, Whitaker and Pigford [81] use beam deflection technique to measure thermodiffusion factor for binary mixtures. In 1960, Agar and Turner [82] was the first who introduced 'ratio-cell' method to measure Soret coefficient. They used 1 cm height cylindrical shaped Soret cell and measured Soret coefficient of similar electrolytes used by Tanner [74; 75; 76]. They used conductimetric technique where movement of electrodes from one half of the cell to another half was measured from the ratio of resistances of the Wheatstone bridge. They further improved 'ratio-cell' and measured Soret coefficient of aqueous solutions [83]. Longworth [84] was the first who introduced interferometry technique to measure Soret coefficient. He used a twin-channel cell which was filled with KCl solution and water solvent separately. The height of the cell was 10 mm or 15 mm and applied temperature difference was 10 °C with various mean temperatures viz. 15, 25, 35 and 45 °C. From his results, convection inside the cell was clearly significant. He claimed that data of Tanner's early work [74] are more reliable than his later work [75].

There is a theoretical value for critical $Ra_c = 1708$ for natural convection in a Rayleigh-Benard cell, given in all heat transfer equations. This concept is very important in designing many convectionless systems including Soret cell for measuring the negative Soret coefficients.

Bobrova and Rabinovich [85] showed that both the Soret and molecular diffusion coefficient can be measured from a single transient experimental technique. They measured diffusion coefficients of aqueous sucrose solution from the change of concentration between top and bottom of the upper heating diffusion circular cell of height 7.75 mm. Concentration was measured by analyzing refractive indices of the collected liquid samples from top and bottom sections. They [86] further worked on measurement of Soret coefficient of Carbon Tetrachloride-Benzene and carbon Tetrachloride-Hexane mixture for wide range of concentration.

For a century, scientists have been trying their best to measure reliable Soret and diffusion coefficient of liquids, however accurate measurement is still missing. Due to non-intrusiveness, interferometry technique has been applied to measure thermodiffusion coefficients for a long time [84; 87]. In last decade, the design of the flow cell used by Thomaes et al has

been upgraded for SCCO (Soret Coefficients of Crude Oils) experiments in FOTON M2 mission in microgravity. Later on, the upgraded Soret cell and optical digital interferometry (ODI) technique based on Mach-Zehnder Interferometry have been used in SoDiUM (Soret and Diffusion Under Microgravity) experiments [88] and DSC (Diffusion and Soret Coefficients) experiments [89] in the SODI facility on board of ISS by Van Vaerenbergh and his coeworkers. The aim of the SoDiUM and DSC experiments was to study both the thermodiffusion and reverse (or pure) diffusion of multicomponent mixtures from the same experiment. The beauty of this technique is that detailed information of transient 2-D temperature and concentration distribution is possible for entire duration of the experiment. Diffusion coefficients can be easily calculated from the temperature and concentration information. Shevtsova and her co-workers [90; 91] applied ODI technique for ground based experiments. So, we have been motivated to adopt and further study of this technique in detail.

Though ODI technique is highly accurate from the technical point of view, it [90] faced some difficulties such as formation of bubbles and convective flow inside the Soret cell. Bubbles may appear inside the cell from any or combination of the following [92]: initially dissolved gas into the liquid, incomplete filling of the cell, invisible small bubbles stacked in the corner or wall of the cell etc. The causes of convective flow inside the diffusion cell are mainly geometry of the cell. Mialdun et al. [90; 93] showed that convective flow can be reduced by reducing the wall thickness of the glass part from 5 mm to 1.3 mm and by reducing the height of the protruded part of the copper plate. However, thin glass wall makes the system more sensitive to the temperature distribution of the surrounding air. So, they enclosed the entire set-up with an insulating box and regulated temperature of the box to the mean temperature of the liquid. After all, they improved the cell design, but could not find out an ideal model to get rid of convective flow in the corner

parts of the cell which causes mixing of binary mixtures in the top and bottom parts of the cell. They [73; 94] further worked on thermal design of the diffusion cell and found that convective flow can be reduced by using inner cell of dimension of 18 mm x 18 mm x 6.3 mm with 2 mm thick glass wall, using a sealing gasket of thermal conductivity closer to glass and improving fitting parameter for image analyses.

2.2.3 Experiments in microgravity environments

As mentioned earlier, thermodiffusion coefficients of liquids are very small in magnitude and difficult to measure in terrestrial conditions. So, microgravity is the ideal place to study thermodiffusion. There are several ways one can obtain microgravity environment. A Drop Tower provides reduced gravity $(10^{-5}g_0)$ only for few seconds, where g_0 is 9.8 ms⁻². Prodi et al. [95] studied thermodiffusion of aerosol in a drop tower. Another possible type of short time microgravity environment is a Parabolic Flight. In parabolic flight, airplane obtains reduced gravity $(10^{-2}g_0)$ for 20 to 25 seconds by following a parabolic path for several times relative to the centre of earth. Spacelab was a space laboratory flown several times using space shuttle which was used for scientific experiments in microgravity environment.

Thermodiffusion has been studied for tin-cobalt system in First Spacelab Payload (FSLP) mission [96], isotopic separation of tin in D1 mission [96], thermodiffusion of molten salts were studied in to two successive missions named D1 and D2 by Bert and Dupuy-Philon [97]. A satellite named EURECA was launched along with 71 experiments as payload on July 31, 1992. It was on orbit at 500 km above the earth surface for 10 days and facilitated to study thermodiffusion in Gold-Tin alloy and isotopic separation of Tin in microgravity environment

[98]. Van Vaerenbergh et al. [99; 100] also measured Soret coefficient of 20 binary organic and aqueous solutions in EURECA and compared with ground based results [50].

FOTON-M3 is an unmanned spacecraft, launched in September 14, 2007 from Kazakhstan. It was on orbit of 300 km above the earth surface for 13 days and carried 43 experiments as payloads. One of the diffusion experiments was in polystyrene-toluene solution [101]. Thermodiffusion of five ternary hydrocarbon mixtures at 35 MPa pressure was done by Srinivasan and Saghir [102]. Other experiments of binary, ternary and four component hydrocarbon mixtures at 5 MPa pressure were also done by Van Vaerenbergh et al [103] in FOTON M3.

International Space Station (ISS) is a satellite which is on orbit 330 to 410 km from earth surface and allows currently six crew members on board to do long term scientific researches. The first component of ISS was launched in 1998 and since then, more components have been added in to it to increase the facilities of performing experiments. However, ISS was not the first space station on orbit. Salyut was the first orbiting space station launched by Soviet Union on April 19, 1971 [104]. Mir was the improvement of Salyut space station launched again by Russians to conduct experiments in microgravity from 1986 to 1996. Spacelab was the earlier space station launched by NASA (National Aeronautics and Space Administration) with collaboration of ESA (European Space Agency) to perform experiments in microgravity.

Columbus module is a European laboratory attached with ISS to perform fluid physics, material science and life science experiments in microgravity. SODI (Selectable Optical Diagnostic Instrument) is a modular instrument located in Microgravity Science Glovebox of Columbus laboratory. Two MZI (Mach-Zehnder Interferometer) are attached with SODI, one of the MZI has two wavelength laser sources of 670 nm and 935 nm and can be translated to allow

multiple experiments. Other MZI of 670 nm laser source is mounted in a fixed position. IVIDIL (Influence of Vibrations on Diffusion in Liquids) was a series of 55 experiments of waterisopropanol mixtures performed on SODI to understand the influence of forced vibration on thermodiffusion process [105; 106; 107; 108]. Another project named DSC (Diffusion and Soret Coefficients) has been operated on board of ISS for measuring Soret coefficients in binary and ternary hydrocarbon mixtures of N-Dodecane ($C_{12}H_{26}$), Isobutylbenzene (IBB) and 1,2,3,4-Tetrahydronaphthalene (THN) [109]. The second part of the SODI-DSC mission named 'DCMIX-2' will be conducted onboard of ISS in 2013 for the binary and ternary mixtures of Cyclohexane (CH), Toluene (T) and Methanol (M). Scientists believe that data from DSC experiments will help for better understanding of crude oils and simulating oil reservoirs.

2.3 Review of theoretical approaches

Development of theoretical modelling of thermodiffusion started after many years of Ludwig and Soret's experimental works. Models with nonequilibrium or irreversible thermodynamics have been considered as more successful than the other existing models. In this model, an energy quantity named 'net heat of transport' along with other known thermodynamic properties of pure liquids is used. Nonequilibrium thermodynamic models are based on the assumption that even in irreversible process, small elementary volumes of the system are in locally equilibrium condition. In this section, a detail theory and concepts about nonequilibrim thermodynamics would be revised from literature and briefly discussed.

Equilibrium state is a static and time independent state of a system where no spontaneous process takes place and all macroscopic quantities remain unchanged [110]. In an isolated

system, entropy reaches in maximum at the equilibrium state and the sum of the entropy changes of all components is equal to zero,

$$\sum_{i} dS_{i} = 0 \tag{2.1}$$

However, if the system is in process of spontaneous change, according to the second law of thermodynamics the system gives only the inequality such that the sum of the entropy changes of all components is greater than zero,

$$\sum_{i} dS_i > 0 \tag{2.2}$$

In steady state condition, macroscopic parameters such as temperature, concentration and pressure of each point of either thermodynamically open or closed system have time independent values. For example, if constant heat flows is applied through a gaseous or liquid mixture, the parameters of the system will be approached time invariant values. So, the theory can then be used to provide a thermodynamic expression to determine the composition gradient across the gas or liquid mixture.

2.3.1 Thomson theory

Thermoelectric device creates electric current in the presence of applied temperature difference in each side and it creates or absorbs heat in each side when electric current is applied to the device. Peltier thermo-electric effect is the heat absorption and rejection at the two electrified junctions of two different metals. This effect is named after French physicist Jean-Charles Peltier (February 22, 1785 to October 27, 1845), who observed it in 1834. On the other hand, another similar heat effect or thermo-electric effect named 'Thomson effect' is the

absorption or evolution of heat when a current flows between two parts of the same metal or conductor (except super conductor) which are maintained at different temperatures.

Thomson effect is named after the British physicist William Thomson or Lord Kelvin (June 26, 1824 to December 17, 1907), who observed it in 1851. Both of the Peltier and Thomson effect are reversible that means they change sign when the direction of current is reversed. From thermodynamic view, the thermo-electric circuit is complicated due to the following two irreversible effects such as heat conduction along the wire and the Joulean heat due to the resistance of the conductor. So, a reversible thermo-electric circuit is formed to which the second law of thermodynamics i.e. equation (2.1) cannot be applied. Thomson applied this equation only to the reversible heat effects at steady state condition of the system. To make the concept clearer, let us consider a virtual flow of current across the liquid. ΔS_p and $\Delta S'_p$ are the entropy changes in the heat reservoirs at the two junctions due to the Peltier heat, ΔS_T and $\Delta S'_T$ are the entropy changes in heat reservoirs located at the end of the two wires due to the Thomson heats. Then, in steady state, Thomson wrote as,

$$\Delta S_p + \Delta S'_p + \Delta S_T + \Delta S'_T = 0 \tag{2.3}$$

This process is considered as reversible because there is no production of entropy. And, the virtual flow of current across the liquid junction creates displacement of ions.

2.3.2 Onsager's theory

Onsager's theory is based on the principle of microscopic reversibility such that under equilibrium condition any molecular process and reverse of that process will be taking place on the average at the same rate, though equilibrium was not maintained in molecular level. If there is no dissipative or thermodynamically open process taking place, equation (2.1) can be applied at the steady state of the system. There are two modes of heat conduction through a system such as 'migration' and 'exchange'. In perfect gas, energy is passed across the system as a migration mode in the form of kinetic and potential (internal) energy of the moving particles. And, in crystalline solid, energy is passed across a system from one particle to another particle as an exchange mode without changing positions in the material. To be in equilibrium condition, system requires following: no overall flow of energy across the system, no overall movement of the substance, but the individual molecules of the material may move to and fro through any cross section.

Let us consider two types of molecules, activated molecules whose energy are greater than a certain amount, say E and deactivated molecules whose energy are lower than E. Macroscopic equilibrium would be possible in the system only if there is a net flow of activated molecules in one direction and equal flow of deactivated molecules in the reverse direction. So, the resultant flow of energy caused by 'migration' in the process would be balanced by an equal and reverse flow of energy caused by 'exchange'. Onsager's theory succeeds in making contact with spontaneous process or with systems in a steady state by means of the 'thermodynamic equations of motion', which express an assumed linearity between the rates of the various types of processes such as energy flow, diffusion etc and the values of the thermodynamic forces which results the corresponding energy flows such as temperature gradients, chemical potential gradients etc.

Let us consider an example of Onsager's theory, where \vec{J}_1 , \vec{J}_2 are the heat flow and electricity flow, \vec{J}_2 is zero in steady state condition; \vec{X}_1 , \vec{X}_2 are the forces proportional to temperature and Electromotive force (E.M.F.). Then, according to the linearity which is supported by experiment, we can write,

$$\vec{J}_1 = L_{11}\vec{X}_1 + L_{12}\vec{X}_2 \tag{2.4}$$

$$\vec{J}_2 = L_{21}\vec{X}_1 + L_{22}\vec{X}_2 \tag{2.5}$$

Where, the coefficients L_{11} , L_{22} are related to the thermal conductivity and electrical conductivity of the material. And, L_{12} , L_{21} represent a coupling or interaction of the heat flow with the electric current, which causes the thermo-electric effect. So, the presence of temperature gradient which is \vec{X}_1 tends to give rise to a flow of electricity, \vec{J}_2 and an E.M.F. On the other hand, \vec{X}_2 tends to give rise to a flow of heat \vec{J}_1 .

There is an assumption of Onsager's theory that the above equations (2.4) and (2.5) can be applied to the 'fluctuations within the equilibrium state'. The application of the principle of 'microscopic reversibility' to these fluctuations leads to the very important reciprocity relation which is valid for even 'non-equilibrium states' as,

$$L_{12} = L_{21} \tag{2.6}$$

It also implies a symmetrical relationship between the effect of the temperature gradient on the flow of electricity and effect of the E.M.F on the flow of heat. So, the linear equations (2.4 and 2.5) together with equation (2.6) are the most important points of Onsager's theory.

The equations help to stretch outwards from the equilibrium state of the system to the regions of the non-equilibrium state. However, this kind of thermodynamics applies only for the systems where there is an interaction of two or more different processes or to any simultaneous processes where there is some mechanism of interaction even though the system is in SS (steady state). If the values of the coefficients $L_{12} = L_{21} = 0$, results become less important or insignificant, because there is no interaction. This theory can be applied in the coupling systems
such as relationship between the velocity constants of a composite set of chemical reactions, interactions between diffusion of charged species and the flow of electric current and another most important scientific process of coupling between diffusion of molecules and heat flow which results to 'thermodiffusion' or 'thermo-osmosis' effect. In thermodiffusion effect, a temperature gradient tends to give rise to a flow of matter and hence a pressure or concentration gradient builds up. In contrary, a diffusion process gives rise to a small temperature difference which is called 'Dufour effect'.

The equations obtained from the Onsager's theory are kinetic which contain coefficients. The coefficients can be determined by actual measurement of rates of the system. However, the expression becomes pure thermodynamic only in SS condition, when the coefficients disappear and thermal and mechanical quantities can be measured independently. The meaning and usefulness of the whole Onsager theory can be made much clearer by applying the theory to the particular realistic system such as 'thermodiffusion'. In thermodiffusion process, the theory allows us: (a) to derive physical relations which can be tested by performing experiments, (b) to highlight the existence of a new thermal quantity named 'heat of transport' which is related to the Peltier heat in thermo-electricity process, and (c) to illustrate the structure of the liquid by measuring the heat of transport. This theory is most useful for all similar type physical situations such as displacement of static equilibrium due to the passes through system of a steady flow of heat, electricity or of some chemical substance.

2.3.3 Thermal migration of fluid through a barrier

Let us consider, a homogeneous system containing n components, temperature gradient and a membrane type porous barrier which allows fluid passage but not the heat flow between two layers. However, such type of membrane is practically impossible and there is heat flow through the membrane, so the second law of thermodynamics cannot be applied. But, according to Thomson's theory, second law of thermodynamics can be applied as there is no dissipative process taking place. A typical experimental set up to validate the theory is shown in figure 2.3.



AA is the membrane; B₁, B₂ Bronze porous disks; C₁, C₂ are housings; G₁, G₂ annular gas access; Bolts H; K is the dividing wall; N is the Perspex holder; R is the Bronze casing; W₁, W₂ are tube for gas access

Figure 2.3 A typical Flow of gases experiment through porous membrane [111] In the stationary state, the process can be considered as in a true equilibrium and can be assumed that the sum of the entropy changes in the system is equal to zero. Now, if we consider the displacement of one mole the fluid from layer 1 to layer 2 through the barrier and further assumption that the pressure in both layers remain unchanged at p_1 and p_2 , the work done on the fluid in that process is $p_1\overline{V_1} - p_2\overline{V_2}$. Where, $\overline{V_1}$ and $\overline{V_2}$ are the molar volumes in layer 1 and 2 respectively, which is the volume occupied by one mole of a substance at a given temperature and pressure. So, if the fluid transfer is carried out without heat absorption from external system, we have from the first law of thermodynamics:

$$\overline{U}_{2} - \overline{U}_{1} + p_{2}\overline{V}_{2} - p_{1}\overline{V}_{1} = 0$$
(2.7)

Or,
$$\overline{H}_1 = \overline{H}_2$$
 (2.8)

Where, \overline{U} 's and \overline{H} 's are the molar internal energies and enthalpies in the layers. Internal energy is the energy required to create the system but excludes the energy to displace the system's surroundings, it has two components such as kinetic and potential energy.

On the other hand, enthalpy is a measure of the total energy including internal energy of a thermodynamic system. The molar volume of the fluid in each layer is same. So,

$$d\overline{H} = \left(\frac{\partial\overline{H}}{\partial T}\right)_p dT + \left(\frac{\partial\overline{H}}{\partial p}\right)_T dp = 0$$
(2.9)

By simplifying we obtain,

$$\left(\frac{\partial T}{\partial p}\right)_{H} = -\frac{\left(\frac{\partial H}{\partial p}\right)_{T}}{\left(\frac{\partial \overline{H}}{\partial T}\right)_{p}} = -\frac{1}{C_{p}} \cdot \left(\frac{\partial \overline{H}}{\partial p}\right)_{T}$$
(2.10)

Where, C_p is the heat capacity and equation (1.10) is the expression for the Joule-Thomson coefficient.

During the fluid transfer period, temperature does not remain constant in each side of the barrier except in the special case where the fluid is able to pass into or out of the barrier with negligible heat effect. Under constant pressure and adiabatic state of the system, enthalpy of the fluid remains same in both sides of the barrier at a given instant and may change over time at the time of fluid transfer. When an element of fluid transfers from layer 1 through the barrier, a quantity of energy has to be removed or provided at the interface. This causes change of enthalpy of the fluid remaining in the layer 1 with a resultant change in the temperature and a similar but opposite effect is expected at the interface between the barrier and layer 2. The dissolving of the fluid at the one side of the barrier will be accompanied by the absorption or evaluation of heat and a corresponding reverse effect when it passes out of the solution at the opposite surface.

If Q_i is the mean energy per mole of component *i* transported by the molecules during their passes across the barrier; Q_i^* is the heat of transport of component *i* which is the amount of heat that Q_i exceeds the enthalpy H_i of the fluid in the vessel from which the transfer takes place. So, Q_i^* is equal to (Q_i-H_i) , if Q_i^* is a finite value, this amount of energy is removed from the fluid remaining in layer 1 and transferred to that contained in layer 2 per mole of fluid passing across. If the pressures and temperature in layer 1 and 2 are p, T and (p+dp), (T+dT) respectively. We are assuming virtual displacement of one mole of fluid from layer 1 to layer 2, where pressures, temperatures and thermodynamic states in each layers remain constant. There is absorption of heat by the fluid from the layers which is the change in its enthalpy per mole due to the change of state. If, dH_i and dS_i are the change of the partial molal enthalpy and entropy of component *i* which is displaced, we have to consider the change as a function of the (n-1) independent mole fractions N_i, as well as pressure and temperature.

There are three types of entropy change during the transfer. First type is the corresponding entropy change in the layer due to absorption of heat,

$$d\overline{S}_{r_1} = -\frac{d\overline{H}_i}{T} = -\frac{1}{T} \left(\frac{\partial \overline{H}_i}{\partial T} . dT + \frac{\partial \overline{H}_i}{\partial p} . dp + \sum \frac{\partial \overline{H}_i}{\partial N_J} . dN_j \right)$$
(2.11)

The second type of entropy change corresponds to transfer of heat Q^* which is absorbed in layer 1 and liberated in layer 2,

$$d\overline{S}_{r_{2}} = -\frac{Q_{i}^{*}}{T} - \left(-\frac{Q_{i}^{*}}{T+dT}\right) = \frac{-Q_{i}^{*}.dT}{T^{2}}$$
(2.12)

Third type of entropy change corresponds to change of its state,

$$d\overline{S}_{f} = \frac{\partial \overline{S}_{i}}{\partial T} dT + \frac{\partial \overline{S}_{i}}{\partial p} dp + \sum \frac{\partial \overline{S}_{i}}{\partial N_{j}} dN_{j}$$
(2.13)

So, according to Thomson's theory which is the assumption of the sum of above mentioned three entropy changes is equal to zero. So,

$$d\overline{S}_{r_1} + d\overline{S}_{r_2} + d\overline{S}_f = 0 \tag{2.14}$$

Equation (2.14) is the equating of the entropy decrease of system to the entropy increase of the fluid, as it was a variation about a state of true equilibrium. By substituting values of equation (2.11), (2.12) and (2.13) in to the equation (2.14) we get,

$$\begin{bmatrix} -\frac{1}{T} \left(\frac{\partial \overline{H}_{i}}{\partial T} . dT + \frac{\partial \overline{H}_{i}}{\partial p} . dp + \sum \frac{\partial \overline{H}_{i}}{\partial N_{j}} . dN_{j} \right) \end{bmatrix} + \begin{bmatrix} -Q_{i}^{*} . dT \\ T^{2} \end{bmatrix} + \begin{bmatrix} \frac{\partial \overline{S}_{i}}{\partial T} . dT + \frac{\partial \overline{S}_{i}}{\partial p} . dp + \sum \frac{\partial \overline{S}_{i}}{\partial N_{j}} . dN_{j} \end{bmatrix} = 0$$
(2.15)

In equation (2.15), the summation has been carried out over the (n-1) mole fractions. After inserting the thermodynamic values of the differential coefficients, equation (2.15) reduces to,

$$\overline{V}_i.dp + \sum \frac{\partial \mu_i}{\partial N_j}.dN_j + \frac{Q_i^*.dT}{T} = 0$$
(2.16)

Where, μ_i is the chemical potential of component *i*. For the special case of single component system, equation (2.16) becomes,

$$\frac{dp}{dT} = -\frac{Q^*}{\overline{V}T} \tag{2.17}$$

Chemical potential is a measure of the potential that a species has to move from 'one phase to another phase' or 'undergoes a chemical reaction'. In 1876, J. William Gibbs [112] provided the concept of the chemical potential μ_i of a species. If there is no chemical reaction, the fundamental equation for the internal energy is,

$$dU = Td\overline{S}_i - pd\overline{V}_i + \sum_i \mu_i . dN_i$$
(2.18)

The first two terms in right hand side of equation (2.18) are the combination of first and second law of thermodynamics. Third term is the additional 'chemical works' for each species and N_i is the amount of species *i*. In an ideal system, the chemical potential of the *i*th component is given by,

$$\mu_i = \mu_i^o(T, p) + RT \log N_i \tag{2.19}$$

By substituting value of μ_i in equation (2.16) we get,

$$\overline{V_i}.dp + RT.d(\log N_i) + \frac{Q_i^*.dT}{T} = 0$$
(2.20)

Equation (2.20) can be applied to thermodiffusion in liquid. For a system with rigid boundaries, the pressure variation is negligible i.e. $\overline{V_i}.dp = 0$.So, equation (2.20) becomes,

$$\frac{d(\log N_i)}{dT} = \frac{Q_i^*}{RT^2}$$
(2.21)

From, equation (2.21), we can see that the variation of composition along temperature gradient can be shown as a function of 'heat of transport' of the particular component. For binary system, the relative separation can be expressed in terms of Soret coefficient,

$$S_{T} = -\frac{d\left(\log\frac{N_{1}}{N_{2}}\right)}{dT} = \frac{Q_{1}^{*} - Q_{2}^{*}}{RT^{2}}$$
(2.22)

Point to be noted that $\sum N_i = 1$ and $\sum N_i Q_i^* = 0$. Also, the total energy flow from layer 1 to layer 2 in the system is equal to the flow of the molecules multiplied by their average energy to the layer 1 of the system.

2.3.4 Wirtz's theory and kinetic interpretation of thermodiffusion

In 1948, Wirtz [113] provided a kinetic interpretation of the 'heat of transport' for explaining thermodiffusion in liquids and solids of the same two layered system separated or divided by a plane as considered in previous section. He considered that the jumping or diffusion of molecules across the dividing plane between the layers as an exponential function of temperature. At stationary state, activated jumping of molecules in one direction is equal to the number of activated jumps in opposite direction. However, as the temperature across the layers is not same, the fraction of activated jump and also the number of available holes is not the same in each layer. Thus, the resulting equation provides the change of composition along the temperature gradient. If q_h is the energy of a molecule required for making an activated jump between two points for the elongation of its thermal vibration and q_l is the energy of a molecule required for creation of hole. The total activation energy E for the process of diffusion is equal to (q_h+q_l) . And, according to Wirtz the heat of transport,

$$Q^* = q_h - q_l \tag{2.23}$$

In stationary state, the rates of jumping molecules of binary mixtures with components 1 and 2 across the dividing plane are,

$$\frac{d(\ln c_1)}{dT} = \frac{-(q_{h_1} - q_{l_1})}{RT^2}$$
(2.24)

And,
$$\frac{d(\ln c_2)}{dT} = \frac{-(q_{h_2} - q_{l_2})}{RT^2}$$
 (2.25)

Where, c_1 and c_2 are the mole fractions per unit volume. So, the Soret coefficient,

$$S_{T} = -\frac{d\left(\log\frac{c_{1}}{c_{2}}\right)}{dT} = \frac{\left(q_{h_{1}} - q_{l_{1}}\right) - \left(q_{h_{2}} - q_{l_{2}}\right)}{RT^{2}}$$
(2.26)

To derive equation (2.23), following assumptions have been considered: (1) before jump, the molecule is at one side of the dividing plane and hole is at the other side of the plane, (2) after jump their positions were reversed, (3) the molecule and hole flow is opposite direction to each other, (4) energies q_h and q_l have to be given in two different temperature such as T and (T+dT). Also, the amount of absorbed energy in one layer is given up when the fluid arrives in another layer, otherwise energy will not be conserved. So, Q^{*} is constant across the two adjacent layers, but dependent on temperature and pressure. For further transfer of molecules from the layer of temperature (T+dT) to the layer of temperature (T+2dT), the energy (Q^{*}+dQ^{*}) would be required. If, E and Q^{*} can be measured experimentally, q_h and q_l can provide the information about the molecular structure of the liquids.

2.3.5 Nonequilibrium thermodynamics

There are numerous thermodynamic models available; most of these models are divided in to two major categories such as independent models and matching parameter models [18]. The matching parameter models work on the basis of physical and thermodynamic properties of the mixture. For multi-component mixtures, mass flux of *i*th component can be expressed using irreversible thermodynamics [114; 115] as,

$$\vec{J}_{i} = -\sum_{k=1}^{p} L_{ik} \left[\frac{Q_{k} - \overline{H}_{k}}{T_{0}} \vec{\nabla}T + \sum_{j=1}^{p-1} \left(\frac{\partial \mu_{k}}{\partial x_{j}} \right) \vec{\nabla}x_{j} \right]$$
(2.27)

Where, L_{ik} is the phenomenological coefficient, Q_i is the heat of transport of the *i*th component, \overline{H}_k is the partial molar enthalpy and *p* is the number of total components.

In 1952, Denbigh [116] provided the first nonequilibrium thermodynamic model of Soret coefficient (S_T) based on the heat transport concept. Onsagar's famous reciprocal relations [117; 118] were used in the nonequilibrium thermodynamics model. The magnitude of the Soret coefficient of non-polar binary mixtures was expressed by the heats of transport of the components using first and second law of thermodynamics as,

$$S_{T} = \frac{-d}{dT} \left(\ln \left[\frac{x_{1}}{x_{2}} \right] \right) = \frac{Q_{1}^{*} - Q_{2}^{*}}{RT^{2}}$$
(2.28)

Where, x_1 , x_2 are the mole fractions of component 1, 2; *T* is the mean temperature; R is the gas constant; Q_1^* is the heat of transport or energy transported across a reference plane per mole of component 1 when $\nabla T = 0$ and component 2 is stationary. If both of the molecules of component 1 and 2 are equal in size, there is a certain amount of energy must be provided by the

neighbour molecules for detaching one mole of component 1 from left plane to the right plane. This energy is,

$$W_{H_1} = \frac{-zNf}{2} \left(x_1 w_{11} + x_2 w_{12} \right)$$
(2.29)

Where, *N* is the Avogadro number, *f* is the fraction of bonds broken up during the jump of the molecule which is less than unity, w_{11} and w_{12} are the potential energies of the pair of molecules 1-1 and 1-2. The amount of energy required for one mole of component 2 is,

$$W_{H_2} = \frac{-zNf}{2} \left(x_2 w_{22} + x_1 w_{12} \right)$$
(2.30)

Where, w_{22} is the potential energies of the pair of molecules 2-2. At the time of jumping, the mean energy given up to the system for filling up the holes by components 1 and 2 is,

$$W_{L} = x_{1}W_{H_{1}} + x_{2}W_{H_{2}} = \frac{-zNf}{2} \left(x_{1}^{2}w_{11} + 2x_{1}x_{2}w_{12} + x_{2}^{2}w_{22} \right)$$
(2.31)

To maintain constant temperature and pressure in the system, certain amount of heat namely 'heat of transport' of each component is required to be supplied to the system, which is defined by Denbigh for component 1 as,

$$Q_1^* = W_{H_1} - W_L = \frac{-zNf}{2} x_2 [x_1(w_{11} - w_{12}) - x_2(w_{22} - w_{12})]$$
(2.32)

Similarly, the 'heat of transport' of component 2 is,

$$Q_2^* = W_{H_2} - W_L = \frac{-zNf}{2} x_1 [x_2 (w_{22} - w_{12}) - x_1 (w_{11} - w_{12})]$$
(2.33)

Using equations (2.32) and (2.33), Denbigh showed that the thermodynamic state satisfy which is,

$$x_1 Q_1^* + x_2 Q_2^* = 0 (2.34)$$

From equation (2.34), it is clear that there is no absorption of heat while both of the molecules of component 1 and 2 move in the same direction i.e. the composition remain unchanged. According to Denbigh, the Soret coefficient can be obtained using chemical potential, which is

$$\mu_{1} = f(T, p) + RT \ln x_{1} + (1 - x_{1})^{2} \frac{zN}{2} (2w_{12} - w_{11} - w_{22})$$
(2.35)

For ideal solution, $2w_{12}=w_{11}+w_{22}$. So, equation (2.35) reduces to,

$$\mu_1 = f(T, p) + RT \ln x_1 \tag{2.36}$$

$$\mu_2 = f(T, p) + RT \ln x_2 \tag{2.37}$$

So,

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p} = \frac{RT}{x_1}$$
(2.38)

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,p} = \frac{RT}{x_2}$$
(2.39)

We also know that

$$\frac{d\ln x_1}{dT} = \frac{-Q_1^*}{T\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p}}$$
(2.40)

And,

$$\frac{d\ln x_2}{dT} = \frac{-Q_2^*}{T\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,p}}$$
(2.41)

So, the Soret coefficient,

$$S_{T} = \frac{-d}{dT} \left(\ln \left[\frac{x_{1}}{x_{2}} \right] \right) = \frac{Q_{1}^{*} - Q_{2}^{*}}{RT^{2}}$$
(2.42)

In 1954, Rutherford and Drickamer [119] improved Denbigh's regular model by adding correction factors for size and shape of the molecules. Their expression required number of molecules moving into a hole left by another molecule as that jumps into another hole. For the regular solution, they simply rearranged equation (2.42) to have an expression of thermodiffusion factor $\alpha_{\rm T}$ as,

$$\alpha_T = \frac{Q_2^* - Q_1^*}{x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p}}$$
(2.43)

From 1955 to 1956, the non-equilibrium thermodynamic model was established by Drickamer and his co-workers [115; 120; 121], they correlated the net heat of transport with the concept of heats of vaporization, excess energy, entropy and volume of mixing [115]. They later added the activation energy of viscous flow [120] and partial molar activation energy of viscous flow [121]. According to them, the thermodiffusion factor is

$$\alpha_{T} = \frac{\overline{V_{1}}\overline{V_{2}}}{\overline{V}x_{1}} \left[\frac{\partial\mu_{1}}{\partial x_{1}} \right]_{T,p} \left[\frac{Q_{2}^{*}}{\overline{V_{2}}} - \frac{Q_{1}^{*}}{\overline{V_{1}}} \right]$$
(2.44)

Where, $\overline{V_1}$, $\overline{V_2}$ are the partial molar volumes and $\overline{V} = x_1 \overline{V_1} + x_2 \overline{V_2}$ is molar volume.

From 1959 to 1963, Rutherford and his co-workers further used the theory of Rutherford and his co-workers for Methane-n-Butane binary mixture in critical region [122] and both of the critical and liquid regions [123]. In 1986, Guy [124] provided another model of thermodiffusion factor based on nonequilibrium thermodynamics, which requires partial molar excess energy of the pure components. Their model was found good agreement with experimental data of nonelectrolyte liquids. In 2004, Shapiro [125] provided a model based on the statistical theory of fluctuations around an equilibrium state in a two macroscopic reservoir system of calculating thermodiffusion factor in multicomponent mixtures.

In 1950, Haase provided a model for thermodiffusion factor based on the analogy of mass transfer due to the pressure and temperature gradient. Later on in 1989, Kempers [126] provided theoretical expressions based on nonequilibrium thermodynamics of Haase's model and provided the concept of 'frame of reference' in thermodiffusion. He expressed the modelling using two bulb systems and claimed that thermodiffusion factor can be calculated using single equation of state (EOS) only. However, later on it was found that both Haase's and Kempers's models contain lot of errors. In 1980, Mortimer and Eyring [127] provided a model based on the elementary transition state theory, which was tested for the earlier experimental data of Saxton et al. [41] using nonlinear regression analysis. The model is applicable only to the mixtures of molecules with equal sizes and no further follow up works have been reported of this model. In 2005, another model based on hydrodynamic and Brownian motion has been developed by Brenner and Bielenberg [128; 129] for thermophoresis of particles in liquids.

In last decade, Firoozabadi and his coworkers [114] improved the earlier thermodynamic of irreversible based model by adding Peng-Robinson equation of state (PR-EOS) for both binary and multicomponent mixtures. Recently, Saghir and his coworkers [130] extended the model for the feasibility of different EOS for different types of mixtures. Although there is no universal model to predict the thermodiffusion coefficient for all types of binary mixtures, Shukla and Firoozabaadi [114] showed that their model along with PR-EOS is the best of predicting thermodiffusion coefficient in hydrocarbon mixtures for any pressure, but away from the critical zone. For binary mixture, L_{12} and L_{11} are independent and composition gradient resulting from the temperature gradient in the steady state for the first component can be written from equation (2.1) as,

$$\frac{\nabla x_1}{x_1} = -\left[\frac{Q_1^*}{x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)}\right] \left(\frac{\nabla T}{T_0}\right)$$
(2.45)

$$\frac{\nabla x_1}{x_2} = -\left[\frac{Q_2^*}{x_2\left(\frac{\partial \mu_2}{\partial x_1}\right)}\right] \left(\frac{\nabla T}{T_0}\right)$$
(2.46)

Where, $Q_i^* = Q_i - \overline{H}_i$ is the net heat of transport. Using Gibbs-Duhem equations ($\sum x_i d\mu_i = 0$), thermal diffusion factor (α_T) can be expressed from equation (2.45) and (2.46) as a function of net heat of transport and chemical potential,

$$\alpha_{T} = \left[\frac{Q_{2}^{*} - Q_{1}^{*}}{x_{1}\left(\frac{\partial \mu_{1}}{\partial x_{1}}\right)}\right]$$
(2.47)

Using the partial molar internal energies (\overline{U}_i) , τ_i which is the ratio of energy of evaporation (ΔU_i^{vap}) to the energy of viscous flow (ΔU_i^{visc}), the chemical potential (μ_k) and the partial molar volume (V_i), thermal diffusion factor of component 1 can be expressed as,

$$\alpha_{T} = \left[\frac{\overline{U}_{1}}{\tau_{1}} - \frac{\overline{U}_{2}}{\tau_{2}}}{x_{1} \left(\frac{\partial \mu_{1}}{\partial x_{1}} \right)_{T,p}} + \frac{\left(\overline{V}_{2} - \overline{V}_{1} \right) \left(\frac{x_{1} \overline{U}_{1}}{\tau_{1}} + \frac{x_{2} \overline{U}_{2}}{\tau_{2}} \right)}{\left(x_{1} \overline{V}_{1} + x_{2} \overline{V}_{2} \right) x_{1} \left(\frac{\partial \mu_{1}}{\partial x_{1}} \right)_{T,p}} \right]$$
(2.48)

Thermal diffusion factor is related to the thermodiffusion coefficient and molecular diffusion coefficient as,

$$\alpha_T = T_0 S_T = T_0 \frac{D_T}{D_M}$$
(2.49)

As mentioned by Shukla and Firoozabadi [114], equation (2.48) cannot be applied to isotropic mixtures unless it has been modified. The theory of calculating energy of viscous flow (ΔU_i^{visc}) is not well established and values of τ can be varied from 3 to 5. So, in order to calculate thermodiffusion coefficient (D_T) from equation (2.49), molecular diffusion coefficient (D_M) needs to be calculated from equation. Following the method of Firoozabadi and his coworkers [131; 132], the molecular diffusion coefficient (D_{Mik}) can be calculated. The method is revised and discussed here briefly for multicomponent mixtures. Maxwell-Stefan expression for the molar diffusive mass flux of non-ideal systems is,

$$\vec{J} = -\frac{c\Gamma}{\vec{B}}\vec{\nabla}c \tag{2.50}$$

Where, c is the molar density of the mixture, \vec{B} is the square matrix of order (p-1) with elements of,

$$\vec{B}_{ii} = \frac{C_i}{\hat{D}_{ip}} + \sum_{\substack{k=1\\i\neq k}}^{p} \frac{C_k}{\hat{D}_{ik}}$$
(2.51)

$$\vec{B}_{ij} = -c_i \left(\frac{1}{\hat{D}_{ij}} - \frac{1}{\hat{D}_{in}} \right)$$
(2.52)

And, Γ is the matrix with elements given by,

$$\Gamma_{ij} = c_i \frac{\partial \ln f_i}{\partial c_j} \Big|_{c_j, T, p}$$
(2.53)

Where, f_i is fugacity of component i, $c_j = c_1$, c_2 ... c_{p-1} . Γ represents fluid mixture nonideality at a given conditions and in the case of nonpolar mixtures, its elements can be calculated using Peng-Robinson equation of state (PR-EOS). On the other hand, the mole based Fickian diffusive flux can be written as,

$$\vec{J} = -cD_{M_k}\vec{\nabla}c \tag{2.54}$$

Where, $D_{M_{k}}$ is the square matrix of order (p-1) of Molecular or Fickian diffusion coefficients. By comparing equation (2.50) and (2.54), the expression for molecular diffusion coefficients can be written as,

$$D_{M_{\vec{k}}} = \frac{\Gamma}{\left(\vec{B}\right)} \tag{2.55}$$

2.3.6 Equation of State (EOS)

Performance of nonequilibrium thermodynamic models depends on the accuracy of thermodynamic properties, which are measured using EOS (equation of state). As mentioned earlier, a universally accepted thermodiffusion theoretical model is still lacking and different models are applied for specific types of liquid mixtures. So, the performance of that model depends on the perfect choosing of EOS as well. In this current research, Peng-Robinson equation of state (PR-EOS) [133] has been used. PR-EOS can be written as,

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$$
(2.56)

Where, p is pressure, T is the temperature, v is the molar volume, a is the temperature dependent attraction parameter, b is the co-volume parameter which refers to the volume occupied by molecules under an infinitely high pressure and R is the universal gas constant. Peng and Robinson rewrote equation (2.56) as,

$$Z^{3} - (1 - B)Z^{2} + (A - 3B^{2} - 2B)Z - (AB - B^{2} - B^{3}) = 0$$
(2.57)

The parameters of equation (2.57) are:

$$A = \frac{ap}{R^2 T^2} \tag{2.58}$$

$$B = \frac{bp}{RT}$$
(2.59)

$$Z = \frac{pv}{RT}$$
(2.60)

Equation (2.57) has three roots corresponds to different phases. At critical point, equation (1.62) provides,

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{p_c}$$
(2.61)

$$b(T_c) = 0.07780 \frac{RT_c}{p_c}$$
(2.62)

$$Z_c = 0.307$$
 (2.63)

Also, at the temperature other than critical point,

$$a(T) = a(T_c)\alpha(T_r.\omega)$$
(2.64)

$$b(T) = b(T_c) \tag{2.65}$$

 α of equation (1.65) is a non-dimensional term which is a function of reduced temperature T_r and acentric factor ω . The relationship between α and T_r is,

$$\sqrt{a} = 1 + \kappa \left(1 - \sqrt{T_r} \right) \tag{2.66}$$

Where, κ is a constant of each pure substance correlated against acentric factor α as,

$$\kappa = 0.37464 + 1.54226\omega - 26992\omega^2 \tag{2.67}$$

The parameters used in equation (2.57) are pure component parameters and defined using following mixing rules:

$$a = \sum_{i} \sum_{j} x_i x_j a_{ij}$$
(2.68)

$$b = \sum_{i} x_i b_i \tag{2.69}$$

Where, x_i is the mole fraction, a_{ij} of equation (2.68) is

$$a_{ij} = \left(1 - \delta_{ij}\right) \sqrt{a_i a_j} \tag{2.70}$$

Where, δ_{ij} of equation (2.70) is the binary interaction parameter between *i*th and *j*th component. For simplicity, the values of δ_{ij} in this current study are assumed to be zero.

2.4 Summaries

Based on the brief literature review, it is clear that in terrestrial condition, a good experimental method must have the following criterions: (a) thermal and diffusion characteristic time should be as small as possible. Otherwise, the duration of the experiment would be very long i.e. few weeks. So, the characteristic length (height of the diffusion cell) should not be too

long, but should be large enough such as 5 to 10 mm to visualize the mass separation; (b) whole system should have uniform temperature distribution and free from disturbance of convective flow. Though in ground based experiments, convection is unavoidable due to the presence of gravitational force, some of the special conditions can reduce the chances of convection such as maintaining the system into small temperature gradient, heating from top of the diffusion cell, proper thermal design of Soret cell, placing the diffusion cell perfectly horizontal etc; (c) system should be non-intrusive and remotely measurable, this criterion can be achieved by adopting optical techniques; (d) method should be applicable for wide range of concentration and mixtures; (e) temperature of the diffusion cell should be controlled with high precision i.e. less than ±0.02 K; (f) to avoid Marangoni convection, completely filling of the diffusion cell is required. Among all of the experimental methods, because of non-intrusiveness and absence of any mechanically driven or any moving parts, the convectionless systems having optical methods are more favorable. The only limitation is that the liquid must be transparent to the optical sources i.e. laser beams. Though, there is no universally accepted theoretical models available, models based non-equilibrium thermodynamics are considered as more developed at least for binary liquid mixtures.

Chapter 3

Materials and experimental methods

3.1 Fluid materials

All of the chemicals used for the experiments have been purchased from 'Fisher Scientific Canada'. Binary mixtures have been prepared in room temperature from the pure components of Decane, Dodecane, Isobutylbenzene and 1,2,3,4-Tetrahydronapthalene (Fisher Scientific catalogue numbers of O2128500, O2666500, AC150965000 and AC146730010) having purities of more than 98%. The mass of the liquid mixtures have been measured with a Denver Summit Series Instrument balance (Fisher Scientific catalogue numbers of SI-234) with precision of 4 decimal places (10⁻³ gm). Mixtures have been prepared in air tight glass bottles and used within a week to avoid possible change of composition due to evaporation. Before using, liquid mixtures have been mixed properly using magnetic stirrer at 200 rpm.

3.2 Experimental methods

The principle of Mach-Zehnder interferometer is used for measuring diffusion coefficients. In this technique, a pattern of interference is created by superposition of two light waves. The arrangement of Mach-Zehnder interferometer is shown in figure 3.1. It consists of two beam splitters and two flat mirrors. Beam splitters have been bought from Melles Griot company (BS1-633-50-2025-45P, material: BK7 glass), front surface of it exhibits almost 50±5.0% reflection at 45° angle of incidence. The diameter and thickness of the beam splitters are 50.8 mm and 6.35 mm respectively. Flat mirrors have been bought from Melles Griot (EAV-PM-2037-C, material: crown glass, N-BK7) as well, which have average reflectance of more

than 92% for the visible spectrum range of 450 nm to 650 nm and coated with enhanced aluminum. The aperture of the mirror is 50.8 mm and thickness is 9 mm. Two adjustable mirror mounts (200-20M-3SC-LK) have been used for clamping and adjusting of mirrors.

A red cylindrical He-Ne laser (Melles Griot model: 25-LHP-151-249, beam diameter: 0.8 mm) having wavelength of 632.9 nm and 15 mW power is used as an optical light source. An additional Hitachi semiconductor red laser diode at wavelength of 639 nm is used on the figure 3.1. These wavelengths are visible and provide a significant advantage for the alignment of set up by moving mirrors and beam splitters. Incoming laser beam of coherent light splits into two identical beams of equal intensities at the beam splitter BS_1 . Each of these two beams travels a different path of BS_1 - M_1 - BS_2 and BS_1 - M_2 - BS_2 , until they recombine in another beam splitter BS_2 before arriving at a detector sensor or CCD camera. The difference in the distance or different path lengths and the medium or different refractive indexes travelled by each beams create a phase difference. This phase difference creates the interference pattern from the second beam splitter BS₂ up to the CCD camera. The interference patterns are recorded by the CCD (JAI progressive scan, model: CV-M4-CL+ monochrome digital megapixel camera), which is directly connected with a computer. The resolution of the CCD camera is 1380 x 1030 pixels and the image scale is approximately 6.45 µm square pixel. A pin-hole and a micro-lens are placed in front of the laser source to increase its optical cross-sectional area by expanding the beam which needs to be collimated. So, a plano-convex spherical lens is placed at a distance of its focal length such as 60 cm from the beam expander, which was confirmed by testing the beam using a shear-plate collimation tester (Melles Griot model: 09SPM001). To avoid saturation of CCD camera, the intensity of the laser beam was reduced to the tolerable range of 0 to 255 gray scales using optical density filters.

The second plano-convex lens assists the camera for perfect focusing on the liquid sample to avoid beam deflection error. The thermodiffusion cell containing liquid sample which is transparent to laser beam is placed between M_2 and BS_2 . Thermodiffusion cell was seated and screwed rigidly on top of a rail-jack system. Using rail and jack system, vertical and horizontal positioning of the cell becomes easier. The whole set up is mounted on a 'RS2000 series' tuned vibration damping optical table (Newport corporation, dimension $1.2 \times 2.4 \times 0.203$ m, model: M-RS2000-48-8).



Figure 3.1 Schematic view of the MZI set up

Before starting the diffusion experiment, copper and glass parts of diffusion cell have been unclamped, it was then cleaned using pure acetone and was kept inside a fume hood for few hours. After drying, copper and glass part have been clamped carefully with plastic screws and diffusion cell has been filled up by injecting liquid from a syringe through a plastic pipe. Special care has been taken to make sure that there is no air bubbles inside the cell, which is the most challenging part of the experiment. After filling up, at first top part of the cell was sealed by a metallic screw, then the cell was flipped 90° angle to seal another part using another screw. Thin Teflon tape was patched on the metallic screws to seal the liquid properly. For sealing the liquid between the glass and copper blocks, four Buna-N o-rings have been used. After each experiment, all of the o-rings have been replaced by new o-rings. Then, the cell has been covered with Teflon for thermal insulation and is placed into the Mach-Zehnder interferometer. Finally, the cell has been sandwiched with two Peltier elements as shown in figure 3.2, equipped with electronic proportional-integral-derivative (PID) temperature controllers which are used for switching and maintaining the temperatures of the two copper plates.



Figure 3.2 Block diagram of Soret cell

Temperatures of the both copper plates have been measured using two individual thermistors placed in a groove close to the liquid-copper interface. One side of each Peltier element has been sandwiched with diffusion cell and another side with a thermostatted water bath. Copper plates have been heated or cooled by Peltier and water bath assists Peltier for controlling the temperatures properly by adding or removing heat from outer surface of the Peltier. The precision of the PID temperature controller and the thermostatted bath (Fisher Scientific of model: Isotemp 3016D) are less than ± 0.01 K. Before start grabbing images using the CCD camera, alignment and contrast of the fringes have been checked. The fringes have been aligned horizontally to make easier of data analysis. Fringes have been checked to have at

least seven or eight pixels in between two successive brightest or darkest fringes. To minimize the effect of convection inside the diffusion cell, the top copper block has been maintained at higher temperature than the bottom copper block. Initially, temperatures of both copper plates have been maintained at the mean temperature for twenty minutes. Then, the temperatures of the top and bottom plates have been changed to introduce a temperature gradient which causes segregation of the components in the mixture. So, both the temperature and concentration gradients of the mixture lead to a refractive index gradient which can be measured from calculating the changes of phases of the images.

To avoid convection, the applied temperature difference, $\Delta T = 2$ °K has been used. The reason of using low temperature difference has been discussed in section 4.1. After six to eight hours of operation, the system reaches in steady state condition and maximum segregation of components between top and bottom walls has been occurred due to the Soret (thermodiffusion) effect. Then, the temperature of both Peltier have been switched to the mean temperature, which causes zero temperature gradient i.e. $\Delta T = 0$ between the top and bottom parts of the diffusion cell. After that time, the active concentration gradient of the liquid volume tries to be homogeneous due to the molecular or Fick's diffusion. Fringe images have been continuously recorded for eight more hours at a time step of one minute. After completing the experiment, recorded images have been processed to calculate transport coefficients as discussed in next section.

3.3 Image processing

Fringe images contain all of the information of any physical change of the interferometer through shifting of phase which needs to be measured. Two main techniques are generally used to achieve phase measurement such as phase-shifting method and the Fourier transforms method [134]. Calculation of phase is very easy with phase-shifting method; however, this method needs several phase-shifted images. The Fourier transform method consists of introducing a fringe carrier to extract the fringe phase with Fourier analysis from only one image. This method is much simpler than the phase-shift method which is used for the current study. Phase of the interference fringe images has been calculated by performing following steps: a 2-D fast Fourier transform (FFT) of the fringe images, filtering a selected band of spectrum and doing the inverse Fourier transform. This technique has been adopted from the literature [135]. Interference fringes are directly related to the difference between the shapes of the reference beam and object beam that passes through the sample. This difference can be seen through interference fringes.

3.3.1 Fast Fourier transforms (FFT)

The intensities of the monochrome fringe patterns are recorded by the CCD camera along a rectangular array of 1380 x 1030 pixels, gray scale values ranging between 0 to 255 and 8 bits. The measured intensity I(x, y) can be written as [135; 136; 137],

$$I(x, y) = b(x, y) + a(x, y) \cos[\varphi(x, y)]$$
(3.1)

Where, b(x, y) is the background intensity of the interferogram which may be developed from illumination of the object or bad exposure. a(x, y) is the variation of intensity caused by local contrast of the fringe pattern and $\varphi(x, y)$ is the phase of the intensity I(x, y) which needs to be determined from equation (3.1). One very important thing which needs to be care is that the cosine function of equation (3.1) is a periodic and even function. So,

$$\cos[\varphi(x, y)] = \cos[2\pi n + s\varphi(x, y)]$$
(3.2)

Where, n is an additive integer and $s \in \{-1,+1\}$ is the sign of the cosine.

Now, equation (3.1) can be modified as follow:

$$I(x, y) = b(x, y) + a(x, y) \left[\frac{1}{2} \left(e^{i\phi(x, y)} + e^{-i\phi(x, y)} \right) \right]$$
(3.3)

Where, $\cos[\varphi(x, y)]$ is replaced by $\frac{1}{2} (e^{i\varphi(x, y)} + e^{-i\varphi(x, y)}).$

So, equation (3.3) can be written as

$$I(x, y) = b(x, y) + \frac{1}{2}a(x, y)e^{i\phi(x, y)} + \frac{1}{2}a(x, y)e^{-i\phi(x, y)} \text{ and more simplified form as,}$$
$$I(x, y) = b(x, y) + C(x, y) + C^*(x, y)$$
(3.4)

Where, $C(x, y) = \frac{1}{2}a(x, y)e^{i\varphi(x, y)}$, $i = \sqrt{-1}$ and * denotes the complex conjugate.

Now, equation (3.4) needs to be Fourier transformed.

One dimensional Fourier transform of equation (3.4) with respect to x axis can be written as

$$I(u, y) = b(u, y) + C(u, y) + C^*(u, y)$$
(3.5)

One dimensional Fourier transform with respect to y axis can be written as

$$I(x,v) = b(x,v) + C(x,v) + C^{*}(x,v)$$
(3.6)

Or in two dimensional form

$$I(u,v) = b(u,v) + C(u,v) + C*(u,v)$$
(3.7)

In practice, the background intensity 'b' varies slowly compared with the fringe spacing. So, the amplitude spectrum will be a trimodal function with 'b' broadening the zero peak and C and C* placed symmetrically to the origin. Next step is to filter out the zero peaks and one of the two symmetrical parts, let say C*. The filtered amplitude spectrum contains only the complex function C(u, v). If we do the inverse Fourier transform, C(x, y) can be obtained. As C(x, y) is a complex function, we can write it as below

$$C(x, y) = \operatorname{Re}[C(x, y)] + i.\operatorname{Im}[C(x, y)]$$
(3.8)

Where, Re[C(x, y)] and Im[C(x, y)] denote the real and imaginary part respectively of C(x, y). So, the interference phase can be calculated from equation (3.8) as,

$$\varphi(x, y) = \tan^{-1}\left\{\frac{\operatorname{Im}[C(x, y)]}{\operatorname{Re}[C(x, y)]}\right\}$$
(3.9)

In this present study, we would like to calculate the temperature and concentration distributions from the phase shifts. So, we need only the relative values of the phase which is the phase differences of all images from the very first recorded image. Thus, phase difference of all images in 2-D points is,

$$\Delta \varphi(x, y, t_i) = \varphi(x, y, t_i) - \varphi(x, y, t_0)$$
(3.10)

Where, $\varphi(x, y, t_i)$ is the phase of *i*th image and $\varphi(x, y, t_0)$ is the very first image or so called reference image. Both of the temperature and concentration distributions inside the liquid vary linearly in the vertical direction only. In addition, we have assumed that the mode of heat transfer inside the liquid is pure conductive. However, there are some possibilities of unwanted convective flow near the lateral walls and end effects which may increase the possible errors of phase shift measurement. To increase the accuracy of the results, corner portions of the images have been cropped out and only central portion of the images has been used. Then, 2-D phase distribution of $\varphi(x, y, t_i)$ has been made into 1-D of $\varphi(y, t_i)$ by making average of phase of the horizontal pixels.

$$\Delta \varphi(\mathbf{y}, t_i) = \frac{1}{n} \sum_{x=1}^{p_x} \Delta \varphi(\mathbf{x}, \mathbf{y}, t_i)$$
(3.11)

Where, p_x is the number of pixels in horizontal direction. Then, the relative deviation of phase of any pixel can be calculated by subtracting phase of that pixel from the central pixel as,

$$\Delta \varphi_{calculated}(y, t_i) = \Delta \varphi(y, t_i) - \Delta \varphi(y_{central}, t_i)$$
(3.12)

The deviation obtained from equation (3.12) is used to calculate the change of refractive index of any pixel or point of the space. In this current study, in-house software based on the above mentioned Fast Fourier technique has been used to extract the phase from the images. The phase difference has been calculated using Matlab code. The transient evolution of phase of a single pixel has been shown in figure 3.3.



Figure 3.3 Transient phase evolution of single pixel of THN-IBB mixture

An example is shown in figure 3.4, where the phase shift is calculated between a target image as shown in figure 3.4a and a reference image as shown in figure 3.4b. The extracted phases from the FFT method are shown in figure 3.4c and 3.4d respectively. The subtraction of

3.4c and 3.4d provides the phase shift between the actual images such as 3.4a and 3.4b. The phase shift which is shown in figure 3.4e. The phase difference between any two points of figure 3.4e can be obtained by plotting the phase of all pixels between those two points. An example is given in figure 3.4f, where the variation of phase along the vertical median direction is plotted. From this plot we can easily calculate the phase difference, $\Delta \varphi$ between top and bottom wall of the Soret cell, which is $5x2\pi = 10\pi$.

3.3.2 Phase unwrapping

The phase difference calculated from equation 3.12 is wrapped phase. That means, the phase is discontinuous and belongs to the range of $-\pi$ to $+\pi$, which needs to be unwrapped. Phase unwrapping can be performed easily, by comparing the wrapped phase of that pixel with phase of previous pixel. To do so, the phase difference between two adjacent pixels needs to be less than π . If we assume that $\varphi(x)$ is a monotonically increasing phase distribution. Then, the phase unwrapping in the one-dimensional case (along the x-coordinate) is given by the following recurrence procedure:

$$n(x_1) = 0,$$

$$n(x_{i}) = \begin{cases} n(x_{i-1}) & \text{if } |\varphi(x_{i}) - \varphi(x_{i-1})| < \pi \\ n(x_{i-1}) + 1 & \text{if } |\varphi(x_{i}) - \varphi(x_{i-1})| \ge \pi \\ & i = 2, 3, \dots \end{cases}$$

$$\varphi_{\text{continous}}(x_i) = \varphi(x_i) + 2\pi n(x_i), \qquad i = 1, 2, \dots$$
(3.13)



(b) reference image

(a) target image



(c) target phase after FFT



(d) reference phase after FFT

median direction for each pixels

45 x 10



(e) phase shift



1 15 2 25 3 35 4 distance in z direction (m)

Figure 3.4 Calculation of phase shift using Fourier transforms method [135]

shift

0.5

For a non-monotonic phase distribution, the phase unwraps is done by the following recurrence procedure:

$$n(x_{i}) = 0,$$

$$n(x_{i}) = \begin{cases} n(x_{i-1}) & \text{if } |\varphi(x_{i}) - \varphi(x_{i-1})| < \pi \\ n(x_{i-1}) + 1 & \text{if } |\varphi(x_{i}) - \varphi(x_{i-1})| \le -\pi \\ n(x_{i-1}) - 1 & \text{if } |\varphi(x_{i}) - \varphi(x_{i-1})| \ge \pi \\ & \text{i} = 2, 3, \dots \end{cases}$$

$$\varphi_{\text{continous}}(x_i) = \varphi(x_i) + 2\pi n(x_i), \qquad i = 1, 2, \dots$$
 (3.14)

From equation 3.14, we can see that the phase remains unchanged if the difference is less than π . However, if the difference is less than $-\pi$, the phase is equal its wrapped phase plus 2π and if the difference is more than π , the phase is equal its wrapped phase minus 2π . In practice, a two-dimensional phase unwrap of equation 3.12 is required for obtaining full information contained in the whole interferogram. For a non-monotonic two-dimensional phase distribution, phase unwrapping is done iteratively in the *x* and *y* coordinate directions by using the following recurrence procedure:

 $n(x_1, y_1) = 0,$

$$n(x_{1}, y_{i}) = \begin{cases} n(x_{1}, y_{i-1}) & \text{if } |\varphi(x_{1}, y_{i}) - \varphi(x_{1}, y_{i-1})| < \pi \\ n(x_{1}, y_{i-1}) + 1 & \text{if } |\varphi(x_{1}, y_{i}) - \varphi(x_{1}, y_{i-1})| \le -\pi \\ n(x_{1}, y_{i-1}) - 1 & \text{if } |\varphi(x_{1}, y_{i}) - \varphi(x_{1}, y_{i-1})| \ge \pi \\ i = 2, 3, \dots \end{cases}$$

$$n(x_{j}, y_{i}) = \begin{cases} n(x_{j-1}, y_{i}) & \text{if } |\varphi(x_{j}, y_{i}) - \varphi(x_{j-1}, y_{i})| < \pi \\ n(x_{j-1}, y_{i}) + 1 & \text{if } |\varphi(x_{j}, y_{i}) - \varphi(x_{j-1}, y_{i})| \leq -\pi \\ n(x_{j-1}, y_{i}) - 1 & \text{if } |\varphi(x_{j}, y_{i}) - \varphi(x_{j-1}, y_{i})| \geq \pi \\ & i = 2, 3, \dots \end{cases}$$

 $\varphi_{\text{continous}}(x_j, y_i) = \varphi(x_j, y_i) + 2\pi n(x_j, y_i), \qquad i, j = 1, 2, \dots$ (3.15)

In this current study, the phase unwrapping was done by using equation 3.15. The unwrapped phase shifts have been used to measure the change of refractive indices. If initial refractive index of $n_o(x, y, t_o)$ has been changed to $n(x, y, t_i)$ due to the change of temperature or concentration or both. Then the change of refractive index is,

$$\Delta n(x, y, t_i) = n(x, y, t_i) - n_o(x, y, t_o)$$
(3.16)

On the other hand, the phase change due to the of refractive index is

$$\Delta \varphi(x, y, t_i) = \frac{2\pi}{\lambda} \int_{l_1}^{l_2} \{ n(x, y, t_i) - n_o(x, y, t_o) \} dl$$
(3.17)

Where, *l* is the optical length or thickness of the sample liquid and λ is the wavelength of the optical source i.e. laser.

By integration we get,

$$\Delta \varphi(x, y, t_i) = \frac{2\pi}{\lambda} \Delta n(x, y, t_i) l$$
(3.18)

Point to be noted that in equation (3.18), $\frac{\partial n}{\partial l}$ is assumed to be zero. If we re-arrange

equation (3.18), we get the expression for change of refractive index as,

$$\Delta n(x, y, t_i) = \frac{\lambda}{2\pi l} \Delta \varphi(x, y, t_i)$$
(3.19)

In isobaric condition, the change of refractive index $\Delta n(x, y, t_i)$ is related to the change of temperature or concentration or both with the following expression,

$$\Delta n(x, y, t) = \left(\frac{\partial n}{\partial C}\right)_{T_o, c_o, \lambda} \Delta C(x, y, t) + \left(\frac{\partial n}{\partial T}\right)_{T_o, c_o, \lambda} \Delta T(x, y, t)$$
(3.20)

3.4 Calibrating of thermistors

The temperatures of the experiments were measured using NTC (negative temperature coefficient) thermistors, which are inexpensive and provide accurate temperature measurement. Thermistors were purchased from Allied Electronics (part number: EC95H303WN), temperature tolerance of it is ± 0.02 °C at a working temperature range of 0 °C to 70 °C. Reference standard supplied by the manufacturer was used. However, to make sure the actual temperature versus resistance values, thermistors were calibrated using Steinhart-Hart R-T equation [138],

$$\frac{1}{T} = e_1 + e_2 (\ln R) + e_3 (\ln R)^3$$
(3.21)

Where, *T* is the temperature in Kelvin, *R* is the resistance in ohm and e_1 , e_2 , e_3 are the three coefficients which need to be measured prior to use. The coefficients have been calculated by measuring resistances of the individual thermistors for three different temperatures such as near the freezing temperature of water, room temperature and boiling temperature of water. Measurements have been repeated for three times for the same mean temperature. Coefficients have been presented in table 3.1.

	Temperature, ^o K	Resistance, ohm (ω)	Coefficients
	075.07	02400	4 67 10-4
	275.37	92400	$e_1 = 4.6/x10^{-1}$
Thermistor 1 (30 Kω at 298 °K)	293.71	35560	$e_2 = 2.99 \times 10^{-4}$
	366.48	2530	$e_3 = -1.71 \times 10^{-7}$
Thermistor 2 (10 Kω at 298 °K)	273.26	304570	$e_1 = 1.16 \times 10^{-3}$
	293.15	126033	$e_2 = 1.52 \times 10^{-4}$
	366.483	7850	$e_3 = 2.91 \times 10^{-7}$

Table 3.1 Coefficients of Steinhart-Hart equation

3.5 Tuning the PID controllers

PID controller is commonly used in control systems such as temperature which calculate 'error' values from the difference between a measured process variable and a desired set point. It automatically minimizes the error by adjusting the process control inputs. The PID controller algorithm involves three separate parameters such as proportional, integral and derivative values, denoted by P, I and D. These values can be interpreted in terms of present error, accumulation of past errors and prediction of future errors based on the current rate of change. By tuning the three constants such as $K_{\rm p}$, $K_{\rm i}$ and $K_{\rm d}$ in the PID controller algorithm, the controller can provide control action designed for specific process requirements.

In 1940, John G. Ziegler and Nathaniel B. Nichols [139] introduced a method for tuning the PID controller. The method is as follow: at first K_i and K_d gains are set to zero, then the *P* gain is increased until it reaches the ultimate gain K_u , at which the output of the loop starts to oscillate. The value of K_u and the oscillation period P_u are used to calculate the PID values as, $K_p = 0.60 Ku, K_i = 0.50 K_p / P_u$ and $K_d = 0.125 K_p P_u$.



Figure 3.5 Block Diagram of the PID controller

Table 3.2	Coefficients	of PID	controller
	Counterents		eomeroniei

	K _p	K _i	K _d
PID controller 1	720	480	750
PID controller 2	60	6.727	371.625

3.6 Summary

In this section, experimental techniques and methodologies have been discussed briefly. The principle of Mach-Zehnder interferometer and image processing technique has been elaborated. Calibrations of thermistors have been performed for accurate measurement of temperature. Temperatures have been tuned by using PID controllers.

Chapter 4

Measurement of refractive indices

4.1 Refractive index

Measurement of refractive indices is very important in various scientific researches such as measurement of purity of liquids, identification of pure liquids and determination of the composition of liquid mixtures [140]. It is also important in designing of laser systems, monitoring of environment pollution and measuring material homogeneity of solidified transparent materials [141]. Measurement of refractive index as a function of wavelength is required in the laser based interferometer systems. Thermodiffusion is a phenomenon of concentration gradient caused by temperature gradient. In recent years, measurement of thermodiffusion coefficients of liquid mixtures using optical digital interferometry technique has been developed [91; 142]. In order to measure thermodiffusion coefficients, accurate measurement of temperature and concentration are required through change of refractive indices with temperature and concentration. Interferometry techniques are ideal for measurement of refractive indices, as these are non-intrusive, high precision and do not require any calibration. Depending on the sample, there are numerous numbers of laser based interferometric techniques available for measuring refractive indices.

Both Mach-Zehnder Interferometer (MZI) and Michelson interferometer (MI) can be used for measurement of refractive indices. However, MZI is superior to MI mainly for two reasons: firstly, the beam of MI passes into the object into two directions such as incoming and returning. Because of changing refractive index, the beam on return does not follow exactly the same path which is called 'differential path error' as shown in figure 4.1. On the other hand,
beams of MZI passes through the object in one direction only. Secondly, fringes of MI are localized on the mirror itself which creates difficulty to make photograph of both fringes and object simultaneously on focus. Whereas, fringes can be made visible in MZI by small tilting of mirrors and object can be focused by placing a lens in front of the camera. In addition, there are some favorable characteristics of MZI [143] such as flexibility of choosing beam spacing and distance between mirrors, beam passes only once through the sample, path difference between beams can be adjusted easily, no major source of errors in refractive index measurement etc.



Figure 4.1 Block diagram of a Michelson interferometer

The so called contrast factors, $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$ and $\left(\frac{\partial n}{\partial c}\right)_{T_0,\lambda}$ of three benchmark mixtures of

C₁₂H₂₆, IBB and THN were measured by Kohler et al. [144; 145] and, Leppa and Wiegand [146]. Where, $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$ is thermal coefficient of refractive indices at constant concentration and

wavelength, and $\left(\frac{\partial n}{\partial c}\right)_{T_0,\lambda}$ is the concentration coefficient of refractive indices at constant

temperature and wavelength.

Based on the literature survey, it has been found that the temperature and concentration coefficient of refractive indices data of some binary mixtures are available. However, simple mathematical correlation of experimental refractive index of the five binary mixtures of $C_{10}H_{22}$ -

IBB, $C_{10}H_{22}$ -THN, $C_{12}H_{26}$ -IBB, $C_{12}H_{26}$ - THN and IBB-THN as a function of concentration, temperature and wide range of wavelength are still missing. In this current study, new correlation is going to be proposed for those mixtures based on the measurement using an Abbemat refractometer. To make sure of the accuracy of the experimental data, comparative measurement of contrast factors using both interferometer and Abbemat refractometer will be discussed.

4.2 Methods

4.2.1 Using MZI

For measuring temperature coefficient of refractive index $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$, a copper box of

outer dimensions 3 cm x 3 cm x 4.5 cm as shown in figure 4.2 is placed in the MZI, which is sandwiched with a Peltier element, equipped with an electronic proportional-integral-derivative (PID) temperature controllers used for switching and maintaining the temperature of the copper plate. The other side of the Peltier element is sandwiched with a thermostatted water bath. The copper box has two grooves of dimensions 1cm x 2cm x 4cm to hold two quartz cells (Helma QS 10 mm). One quartz cell filled with the sample liquid mixture is placed inside of the cubic box. Temperature is measured by using a calibrated NTC thermistor, which has been placed inside the groove of the copper box, close to the copper-quartz interface. When the temperature of the metallic cubic box is varied, images are taken using the CCD camera at every one second interval.

In order to achieve constant heating rate, the temperature interval was extended to ± 5.0 K from the mean (target) temperature. However, only the temperature interval of $T_{mean} \pm 2.0$ K is used for the calculations and the additional data were rejected to avoid error due to convection.

To achieve greater accuracy, temperature of the Peltier element is varied slowly with a maximum power output of 20% only. The dimension of the original images was 1cm x 4cm. However, only central part of the images of dimension 1cm x 2cm has been used for the calculation. The phase changes of the images are calculated individually by performing 2D FFT of the fringe images as described through equation (3.1) to (3.9). Phase shifts of the two dimensional images due to the change of temperature are calculated by subtracting all phase images from the initial image. Change of refractive index, Δn of a single pixel (central pixel or close to the central pixel of 2D phase image) has been calculated from the phase shift $\Delta \varphi$ of that pixel using equation 3.8. Phase shift evaluation with time is shown in figure 4.3. Calculated phase shift was caused by the change of corresponding temperature ΔT of that time period, which is known from the temperature history recorded as text file from the PID controller. Then, $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$ is obtained simply from the ratio of Δn and ΔT .

For measuring concentration coefficient of refractive $index \left(\frac{\partial n}{\partial c}\right)_{T_0,\lambda}$, at first two quartz cells (Helma QS 10 mm) are filled with an initial liquid mixture of same composition and placed inside the copper box. The weights of the liquid mixtures are carefully measured with a Sartorois 1712 balance, with precision of 4 decimal places (10⁻⁴ gm). One of the two quartz cells is used as reference which remains unchanged during the entire experiment. Purpose of using reference cell is to minimize the error due to external vibration and other background noises. Pre-calculated liquid mixture of different composition is injected into the second Quartz cell using a syringe pump (Fisher Scientific catalogue no. 14831200) with a constant injection rate of 0.5 ml per hour and images are taken using the CCD camera at one second time step.



Figure 4.2 Schematic view of the cell for measurement of contrast factor using MZI

The copper box is placed on top of a laboratory magnetic stirrer for instantaneous mixing. The cylindrical shaped micro stirrer bar of size $5 \ge 2$ mm was rotated by magnetic stirrer at a speed of 200 rpm. Before starting injection of the liquid mixture, the injection rate and the total volume of the added solution are given as manual input in to the syringe pump. The mass of the added solution is calculated by multiplying volume with density. Volume of the added solution at mean operating can be measured from syringe pump. Density of the added solution at mean operating

temperature is measured with an Anton Paar DMA 602 U-tube density meter. All the experiments were repeated twice.



Figure 4.3 Phase variation of central pixel due to change of temperature with time

For the calculation, reference and target images have been separated from the original images as shown in figure 4.4(a). The dimension of the original reference and target images was 1cm x 4cm. However, only central part of the images of dimension 1cm x 2cm has been used for the calculation to avoid the possible disturbance caused by the magnetic stir bar. The phase change of both reference and target images are calculated individually by performing 2D FFT of the fringe images, filtering a selected band of spectrum and doing the inverse FFT. Individual phase shifts of both reference and target images are calculated by subtracting all phase images from the initial image.



Figure 4.4 (a) Interference pattern of reference cell in left and target cell in right, (b) phase variation of central pixel due to change of concentration

Final phase shift due to change of concentration has been calculated simply by subtracting of target phase shift from reference phase shift, as shown in figure 4.4(b) (phase shift of a single pixel). Once, refractive index change dn is calculated from phase shift $\Delta \varphi$ using equation (3.19) and concentration change dc is known from injection rate of the syringe pump. Finally, $\left(\frac{\partial n}{\partial c}\right)_{T_0,\lambda}$ is obtained simply from the ratio of Δn and Δc .

4.2.2 Abbe Refractometer

In 1869, German physicist Ernst Abbe created first refractometer and provided details theory and description of it to measure refractive index in a booklet in 1874. This initial version of refractometer had in-built thermometer to measure temperature, water circulating bath to control temperature and analog scale to read the refractive index. The initial version of the Abbe refractometer was upgraded by the German company Carl Zeiss [147]. In latest version of automatic Abbe refractometer, water bath has been replaced by in-built Peltier to heat or cool. Temperature control, refractive index reading display and export of data can be easily controlled through a computer.

Abbemat series are mostly available modern automatic refractometers supplied by Anton Paar. Currently, four types of automatic Abbemat refractometers are available such as the high precision (HP) model, wide range (WR) model, high temperature (WR-HT) model and multiple wavelength (WR-MW) models. Abbemat HP is used in food, beverage and petrochemical industries and medical applications, while Abbemat WR is used for flavors, fragrances, chemicals and pharmaceutical applications. An Abbemat WR-MW model automatic refractometer has been used for the current measurement of refractive index. It provides eight different types of visible wavelengths from 436 nm to 656 nm and wide range of refractive indices from 1.32 nD to 1.72 nD with resolution of 1x10⁻⁶ and accuracy of 4x10⁻⁵. It is free from moving parts and drifts, easy to clean and does not require any maintenance. Major parts are: measuring unit made from waterproof stainless steel of dimension 180mm x 250mm x 120mm, external power supply made from anodized aluminum of dimensions 135mm x 220mm x 80mm, a PC and a RS-232C serial port to interface between measuring unit and PC.

To measure refractive indices, a small amount of sample is placed on the polished surface of the prism which is made from synthetic YAG (Yttrium Aluminum Garnet) material, has close to diamond hardness, scratchproof and corrosion resistant. The sample is covered using a hinged flap and seal of FFKM (Perfluoroelastometer). The sample is irradiated by a LED white light source through filter, lens and prism as shown in figure 4.5, which has been taken from Anton paar brochure [148]. At the liquid-prism interface, the beam either transmitted in to the liquid or reflected back in to the prism. Refractive indices are measured from the critical angle of the total reflection of the beam at desired wavelength. An interference filter is used to tune the wavelength of an accuracy of ± 0.2 nm. Total reflection method provides no influence of colour and turbidity on measurement. A high resolution 2048-element linear CCD array sensor and digital data processing are used to measure the critical angle of total reflection. The sample and prism are thermostatted by in-built solid state Peltier positioned just below the centre of prism, which regulates temperature of the prism-liquid interface of range 10 to 70 °C at a resolution of 0.01 °C. Temperature is measured by PT-1000 temperature sensors at an accuracy of ± 0.03 °C and stability of ± 0.002 °C. The optical system is thermally stabilized at a constant temperature independent of ambient and sample temperature by another solid state Peltier. There is no influence of external vibration on the measurement.



Figure 4.5 Working principle of Abbemat Refractometer [148]

Before doing each experiment, refractometer has been calibrated for known refractive index of distilled water at 20 °C and desired wavelength. After calibration, prism is cleaned using Acetone, wipers have been used to dry the prism immediately. Then, small liquid sample has been placed on the prism, temperature has been set to 19 °C and corresponded refractive index has been recorded. Temperature has been increased at 1 °C step and refractive indices are recorded for that temperature.

4.3 Results

Measured refractive indices at different temperature and wavelength using Abbe refractometer of pure liquids are given in table 4.1 to 4.4. Temperature coefficient of refractive index of individual pure liquids have been calculated using table 4.1 to 4.4 and presented in table 4.5. For measuring concentration coefficient of refractive indices for individual binary mixtures, five samples of different concentrations have been prepared at an accuracy of 1×10^{-3} gm/10 gm or 0.01%. Small sample volume has been placed in the prism and refractive indices for three different temperatures of 20 °C, 25 °C and 30 °C are recorded.

Temperature	Wavelength (nm)					
(°C)	436.1	480.2	546.3	589.3	633.2	657.2
18	1.421975	1.418108	1.414566	1.412868	1.411457	1.410790
20	1.421045	1.417202	1.413515	1.411965	1.410561	1.409890
25	1.418718	1.414929	1.411424	1.409709	1.408336	1.407642
28	1.417313	1.413556	1.410067	1.408347	1.406982	1.406283
30	1.416389	1.412641	1.409157	1.407440	1.406081	1.405386
32	1.415464	1.411719	1.408252	1.406533	1.405177	1.404496
35	1.414074	1.410340	1.406901	1.405186	1.403835	1.403151

Table 4.1 Refractive index of pure C10H22

Temperature and concentration coefficients of refractive indices for binary mixtures are given in table 4.6 and table 4.7 respectively. As compare to the literature data [145; 146] of 633 nm, results obtained from both Abbe refractometer and MZI show good agreement. In addition,

results of MZI show better agreement to the literature data than Abbe refractometer. Because, we had to prepare at least five different samples with error of 1×10^{-3} to measure concentration coefficient of refractive index using Abbe refractometer. On the other hand, MZI technique requires only two samples, one initial sample and another sample for injecting using a Syringe pump. As refractive index (n) is a function of concentration (c), temperature (T) and wavelength (λ), a correlation based on these three parameters would be very helpful for scientific research. Based on our experimental data from Abbe refractometer, we propose a correlation for five binary mixtures as shown in table 4.8. Correlations have been calculated using Microsoft excel data analyses which has been discussed in appendix I. There are several theoretical models or so called mixing rules available in literature to calculate refractive indices of mixtures using physical properties of pure components. One of the popular mixing rules is Lorentz-Lorenz (L-L) [149; 150; 151] model:

$$\frac{n^2 - 1}{n^2 + 2} = \left[\frac{n_1^2 - 1}{n_1^2 + 2}\right] \varphi_1 + \left[\frac{n_2^2 - 1}{n_2^2 + 2}\right] \varphi_2 \tag{4.1}$$

Where, n is the refractive index of mixture and n_1 , n_2 are the refractive indices of pure components. φ_1 , φ_2 are the volume fractions of pure components at a certain temperature and pressure and can be calculated from the relation:

$$\varphi_i = \frac{x_i v_i}{\sum_{i=1}^2 x_i v_i}$$
(4.2)

Where, x_i and v_i are the mole fraction and molar volume of the *i*th component. For calculating refractive indices using mixing rules, refractive indices of pure components of table 4.1 to 4.4 have been used. Differences of calculated refractive indices using proposed correlation and L-L mixing rule are shown from table 4.9 to 4.13.

Temperature	Wavelength (nm)					
(°C)	436.1	480.2	546.3	589.3	633.2	657.2
18	1.431832	1.427866	1.424298	1.422464	1.421000	1.420395
20	1.430938	1.426985	1.423423	1.421602	1.420130	1.419507
25	1.428701	1.424789	1.421234	1.419436	1.417968	1.417334
28	1.427374	1.423469	1.419931	1.418132	1.416677	1.416038
30	1.426486	1.422588	1.419067	1.417259	1.415816	1.415165
32	1.425592	1.421707	1.418202	1.416387	1.414956	1.414295
35	1.424269	1.420387	1.416888	1.415095	1.413674	1.413002

Table 4.2 Refractive index of pure $C_{12}H_{26}$

 Table 4.3 Refractive index of pure IBB

Temperature	Wavelength (nm)					
(°C)	436.1	480.2	546.3	589.3	633.2	657.2
18	1.505344	1.497238	1.490221	1.486637	1.483943	1.482561
20	1.504312	1.496233	1.489228	1.485674	1.482964	1.481594
25	1.501575	1.493727	1.486735	1.483232	1.480512	1.479171
28	1.499950	1.492250	1.485236	1.481760	1.479032	1.477726
30	1.498820	1.491257	1.484231	1.480900	1.478036	1.476754
32	1.497736	1.490270	1.483214	1.479824	1.477033	1.475783
35	1.496166	1.488812	1.481687	1.478354	1.475539	1.474338

Temperature	Wavelength (nm)					
(°C)	436.1	480.2	546.3	589.3	633.2	657.2
18	1.563045	1.554392	1.545638	1.542087	1.538702	1.5375
20	1.562071	1.553428	1.544797	1.541164	1.537794	1.53658
25	1.55967	1.551016	1.542448	1.53882	1.535481	1.534254
28	1.558231	1.549558	1.540996	1.537408	1.534088	1.532816
30	1.557268	1.548581	1.540098	1.536445	1.533166	1.531862
32	1.556295	1.547603	1.539149	1.535488	1.532246	1.530881
35	1.554983	1.546137	1.537800	1.534054	1.530876	1.529435

Table 4.4 Refractive index of pure THN

Table 4.5 Temperature coefficients of refractive index, $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$ of pure components using

Abbemat refractometer

Wavelength	$C_{10}H_{22}$	$C_{12}H_{26}$	IBB	THN
(nm)	(10 ⁻⁴)	(10 ⁻⁴)	(10 ⁻⁴)	(10 ⁻⁴)
436.1	-4.65006	-4.45026	-5.43056	-4.77002
480.2	-4.56844	-4.39896	-4.96155	-4.85456
546.3	-4.46567	-4.3559	-5.01453	-4.64753
589.3	-4.52213	-4.33884	-4.85975	-4.72531
633.2	-4.48482	-4.31056	-4.94132	-4.61193
657.2	-4.49587	-4.34663	-4.83845	-4.74318

Wavelength	C ₁₀ H ₂₂ -IBB	C ₁₀ H ₂₂ -THN	C ₁₂ H ₂₆ -IBB	C ₁₂ H ₂₆ -THN	IBB-THN
(nm)	(10 ⁻⁴)	(10 ⁻⁴)	(10 ⁻⁴)	(10 ⁻⁴)	(10 ⁻⁴)
436.1 ^a	-4.82	-4.84	-4.86	-4.77	-5.14
480.2 ^a	-4.81	-4.78	-4.84	-4.70	-5.02
546.3 ^a	-4.83	-4.70	-4.77	-4.62	-4.91
589.3 ^a	-4.82	-4.74	-4.76	-4.556	-4.956
633.2 ^a	-4.79	-4.71	-4.75	-4.60	-4.98
657.2 ^a	-4.80	-4.67	-4.78	-4.52	-4.85
639 ^b	-	-	-4.42	-4.29	-4.70
632.8 ^c	-	-	-4.51	-4.39	-4.74
633 ^d	-	-	-4.51	-4.41	-4.75

Table 4.6 Temperature coefficients of refractive index, $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$ of (50 wt%) binary mixtures

^aCurrent Study using Abbemat refractometer with maximum error $\pm 3.86 \times 10^{-6}$ ^bCurrent study using Mach-Zehnder interferometer with maximum error $\pm 2.35 \times 10^{-6}$ ^cInterferometry by Wittko and Kohler [145] with maximum error $\pm 2 \times 10^{-6}$ ^dScanning Michelson interferometer by Leppla and Wiegand [146] with maximum error $\pm 9 \times 10^{-7}$

Wave- length (nm)	Mean temperature (°C)	C ₁₀ H ₂₂ -IBB	C ₁₀ H ₂₂ - THN	C ₁₂ H ₂₆ - IBB	C ₁₂ H ₂₆ - THN	IBB- THN
	20	-0.0994	-0.1317	-0.0686	-0.1125	-0.0656
436.1 ^a	25	-0.0995	-0.1314	-0.0688	-0.1133	-0.0670
	30	-0.0991	-0.1315	-0.0681	-0.1137	-0.0669
	20	-0.0632	-0.1245	-0.0655	-0.0974	-0.0430
480.2 ^a	25	-0.0630	-0.1246	-0.0650	-0.0974	-0.0428
	30	-0.0625	-0.1245	-0.0648	-0.0969	-0.0429
	20	-0.0743	-0.1189	-0.0625	-0.1078	-0.0439
546.3 ^a	25	-0.0741	-0.1212	-0.06212	-0.1077	-0.0438
	30	-0.0739	-0.1205	-0.0624	-0.1076	-0.0434
	20	-0.0717	-0.1168	-0.0633	-0.1154	-0.0550
589.3 ^a	25	-0.0684	-0.11674	-0.0677	-0.1156	-0.0538
	30	-0.0688	-0.1153	-0.0681	-0.1156	-0.0544
	20	-0.0685	-0.1154	-0.0646	-0.1129	-0.0548
633.2 ^a	25	-0.0695	-0.1156	-0.0644	-0.1118	-0.0546
	30	-0.0689	-0.1152	-0.0653	-0.1118	-0.0545
	20	-0.0681	-0.1146	-0.0647	-0.1122	-0.0544
657.2 ^a	25	-0.0681	-0.1153	-0.0642	-0.1124	-0.0543
	30	-0.0680	-0.1154	-0.0651	-0.1132	-0.0546
639 ^b	25	-	-	-0.0625	-0.1148	-0.0525
632.8 ^c	25	-	-	-0.0628	-0.1170	-0.0544
633 ^d	25	-	-	-0.0553	-0.1168	-0.0635

Table 4.7 Concentration coefficients of refractive index, $\left(\frac{\partial n}{\partial c}\right)_{c_0,\lambda}$ of (50 wt%) binary mixtures

^aCurrent Study using Abbemat refractometer with maximum error $\pm 5.73 \times 10^{-4}$ ^bCurrent study using Mach-Zehnder interferometer with maximum error $\pm 5.6 \times 10^{-3}$ ^cAbbe refractometer by Wittko and Kohler [145] with maximum error $\pm 4 \times 10^{-4}$ ^dAbbemat refractometer by Leppla and Wiegand [146] with maximum error $\pm 3 \times 10^{-4}$

Table 4.8 Correlation of refractive index (n), concentration (c), temperature (T) and wavelength

(λ) within the range of c = 0.46 to 0.54, T = 20 °C to 30 °C and λ = 436.1 nm to 657

	Equation	Standard error
Mixture		
	(unit of T and λ are °C and nm respectively)	$(n_{experiment} - n_{predicted})$
$C_{10}H_{22}$ -IBB	$n = 1.527 - 0.0647c - 4.784x 10^{-4}T - 6.682x 10^{-5}\lambda$	0.0011
$C_{10}H_{22}$ - THN	$n = 1.583218 \text{-} 0.1205 \text{c} \text{-} 4.6916 \text{x} 10^{\text{-} 4} \text{T} \text{-} 7.68 \text{x} 10^{\text{-} 5} \lambda$	0.0012
	$n = 1.536226 - 0.065304167c - 4.7142x 10^{-4}T$	0.0012
$C_{12}H_{26}$ - IBB		
	$-7.2654 \mathrm{x} 10^{-5} \lambda$	
	$n = 1.577174 - 0.10369c - 4.610633x 10^{-4}T$	0.0012
$C_{12}H_{26}$ - THN	_	
	$-7.282856 \times 10^{-5} \lambda$	
IBB - THN	$n = 1.604063 - 0.052774c - 4.9x10^{-4}T - 9.357x10^{-3}\lambda$	0.0015

Wave-length			Correlation	L-L mixing rule
(nm)	Mean temperature (°C)	Experimental value	$(n_{experiment} - n_{correlation})$	$(n_{experiment} - n_{mixing rule})$
	20	1.457253	1.455948 (9.0x10 ⁻⁴)	1.458873 (-1.1x10 ⁻³)
436.1	25	1.454816	1.453556 (8.7x10 ⁻⁴)	1.456359 (-1.1x10 ⁻³)
	30	1.452571	1.451164 (9.7x10 ⁻⁴)	1.453835 (-8.7x10 ⁻⁴)
	20	1.452164	1.453002 (-5.8x10 ⁻⁴)	1.453137 (-6.7x10 ⁻⁴)
480.2	25	1.449728	1.450610 (-6.1x10 ⁻⁴)	1.450756 (-7.1x10 ⁻⁴)
	30	1.447325	1.448218 (-6.2x10 ⁻⁴)	1.448383 (-7.3x10 ⁻⁴)
	20	1.447052	1.448585 (-1.1x10 ⁻³)	1.447966 (-6.3x10 ⁻⁴)
546.3	25	1.444685	1.446193 (-1.0x10 ⁻³)	1.445691 (-7.0x10 ⁻⁴)
	30	1.442324	1.443801 (-1.0x10 ⁻⁴)	1.443314 (-6.9x10 ⁻⁴)
	20	1.44502	1.445712 (-4.8x10 ⁻⁴)	1.445518 (-3.4x10 ⁻⁴)
590.2	25	1.442598	1.443320 (-5.0x10 ⁻⁴)	1.443175 (-4.0x10 ⁻⁴)
589.5	30	1.440255	1.440928 (-4.7x10 ⁻⁴)	1.440874 (-4.3x10 ⁻⁴)
	20	1.44301	1.442778 (1.6x10 ⁻⁴)	1.443529 (-3.6x10 ⁻⁴)
633.2	25	1.440635	1.440386 (1.7x10 ⁻⁴)	1.441198 (-3.9x10 ⁻⁴)
	30	1.438245	1.437994 (1.7x10 ⁻⁴)	1.438841 (-4.1x10 ⁻⁴)
	20	1.442112	1.441175 (6.5x10 ⁻⁴)	1.442544 (-3.0x10 ⁻⁴)
657.2	25	1.439722	1.438783 (6.5x10 ⁻⁴)	1.440214 (-3.4x10 ⁻⁴)
	30	1.437352	1.436391 (6.7x10 ⁻⁴)	1.437882 (-3.7x10 ⁻⁴)

Table 4.9 Refractive index of $C_{10}H_{22}$ -IBB (50 wt%) using Abbemat refractometer, correlation

Waya longth			Correlation	I I mixing rulo
wave-length	Mean temperature (°C)	Experimental value	Correlation	L-L mixing fule
(nm)			$(n_{experiment}-n_{correlation})$	$(n_{experiment}-n_{mixing rule})$
	20	1.481878	$1.480101 (1.2 \times 10^{-3})$	1.479877 (1.4x10 ⁻³)
436.1	25	1.479438	1.477755 (1.1x10 ⁻³)	1.477476 (1.3x10 ⁻³)
	30	1.477082	1.475409 (1.1x10 ⁻³)	1.475073 (1.4x10 ⁻³)
	20	1.476342	1.476715 (-2.5x10 ⁻⁴)	1.474096 (1.5x10 ⁻³)
480.2	25	1.473976	1.474369 (-2.7x10 ⁻⁴)	1.471724 (1.5x10 ⁻³)
	30	1.471627	1.472024 (-2.7x10 ⁻⁴)	1.469333 (1.6x10 ⁻³)
	20	1.470843	$1.471641 (-5.4 \times 10^{-4})$	$1.468407 (1.7 \text{x} 10^{-3})$
546.3	25	1.468494	1.469295 (-5.5x10 ⁻⁴)	1.46617 (1.6x10 ⁻³)
	30	1.466186	1.466949 (-5.2x10 ⁻⁴)	1.463828 (1.6x10 ⁻³)
	20	1.467042	1.468339 (-8.8x10 ⁻⁴)	$1.466012 (7.0 \times 10^{-3})$
589 3	25	1.464666	1.465994 (-9.1x10 ⁻⁴)	1.46368 (6.7x10 ⁻³)
567.5	30	1.46233	1.463648 (-9.0x10 ⁻⁴)	1.461327 (6.9x10 ⁻³)
	20	1.464867	$1.464969 (-7.0 \times 10^{-4})$	1.46381 (7.2x10 ⁻³)
633.2	25	1.462578	1.462623 (-3.1x10 ⁻⁴)	1.461509 (7.3x10 ⁻³)
	30	1.460252	1.460278 (-1.8x10 ⁻⁴)	1.45919 (7.3 x10 ⁻³)
	20	1.463825	1.463127 (4.8x10 ⁻⁴)	1.462919 (6.2x10 ⁻³)
657.2	25	1.461492	1.460781 (4.9x10 ⁻⁴)	1.460600 (6.1x10 ⁻³)
	30	1.459181	1.458435 (5.1x10 ⁻⁴)	1.458248 (6.4x10 ⁻³)

Table 4.10 Refractive index of $C_{10}H_{22}$ -THN (50 wt%) using Abbemat refractometer, correlation

Wave-length			Correlation	L-L mixing rule
(nm)	Mean temperature (°C)	Experimental value	$(n_{experiment} - n_{correlation})$	$(n_{experiment} - n_{mixing rule})$
	20	1.463364	1.46246 (6.2x10 ⁻⁴)	1.464738 (-9.4 x10 ⁻⁴)
436.1	25	1.460984	1.460103 (6.0x10 ⁻⁴)	1.462278 (-8.9x10 ⁻⁴)
	30	1.458605	1.457746 (5.9x10 ⁻⁴)	1.459822 (-8.3x10 ⁻⁴)
	20	1.457789	1.459256 (-1.0x10 ⁻³)	1.458912 (-7.7x10 ⁻⁴)
480.2	25	1.455433	1.456899 (-1.0x10 ⁻³)	1.456579 (-7.9x10 ⁻⁴)
	30	1.453080	1.454542 (-1.0x10 ⁻³)	1.454259 (-8.1x10 ⁻⁴)
	20	1.452665	1.454454 (-1.2x10 ⁻³)	1.453784 (-7.7x10 ⁻⁴)
546.3	25	1.450334	1.452097 (-1.2x10 ⁻³)	1.45146 (-7.8x10 ⁻⁴)
	30	1.448023	1.44974 (-1.2x10 ⁻³)	1.449143 (-7.7x10 ⁻⁴)
	20	1.450840	1.45133 (-3.4x10 ⁻⁴)	1.451174 (-2.3x10 ⁻⁴)
580.2	25	1.448517	1.448973 (-3.1x10 ⁻⁴)	1.448886 (-2.5x10 ⁻⁴)
389.5	30	1.446165	1.446616 (-3.1x10 ⁻⁴)	1.446642 (-3.3x10 ⁻⁴)
	20	1.448121	1.44814 (-1.3x10 ⁻⁵)	1.449138 (-7.0x10 ⁻⁴)
633.2	25	1.445731	1.445783 (-3.6x10 ⁻⁵)	1.446847 (-7.7x10 ⁻⁴)
	30	1.443370	1.443426 (-3.9x10 ⁻⁵)	1.444551 (-8.2x10 ⁻⁴)
	20	1.447820	1.446397 (9.8 x10 ⁻⁴)	1.448175 (-2.5x10 ⁻⁴)
657.2	25	1.445386	1.444039 (9.3x10 ⁻⁴)	1.445891 (-3.5x10 ⁻⁴)
	30	1.443004	1.441682 (9.2x10 ⁻⁴)	1.443612 (-4.2x10 ⁻⁴)

Table 4.11 Refractive index of $C_{12}H_{26}$ -IBB (50 wt%) using Abbemat refractometer, correlation

Wave-length			Correlation	L-L mixing rule
(nm)	Mean temperature (°C)	Experimental value	$(n_{experiment} - n_{correlation})$	$(n_{experiment}$ - $n_{mixing rule})$
	20	1.487162	1.484346 (1.9x10 ⁻⁴)	1.486467 (4.7x10 ⁻⁴)
436.1	25	1.484680	1.482041 (1.8x10 ⁻³)	1.484135 (3.7x10 ⁻⁴)
	30	1.482288	1.479735 (1.7x10 ⁻³)	1.481816 (3.2x10 ⁻⁴)
	20	1.481344	1.481134 (1.4x10 ⁻⁴)	1.480587 (5.1x10 ⁻⁴)
480.2	25	1.479025	1.478829 (1.3x10 ⁻⁴)	1.478275 (5.1x10 ⁻⁴)
	30	1.476720	1.476524 (1.3x10 ⁻⁴)	1.475951 (5.2x10 ⁻⁴)
	20	1.475719	1.47632 (-4.1x10 ⁻⁴)	1.474935 (5.3x10 ⁻⁴)
546.3	25	1.473429	1.474015 (-4.0x10 ⁻⁴)	1.472655 (5.3x10 ⁻⁴)
	30	1.471152	1.471710 (-3.8x10 ⁻⁴)	1.470386 (5.2x10 ⁻⁴)
	20	1.472135	1.473189 (-7.2x10 ⁻⁴)	1.472367 (-1.6x10 ⁻⁴)
580.2	25	1.469728	1.470883 (-7.9x10 ⁻⁴)	1.470102 (-2.5x10 ⁻⁴)
389.3	30	1.467442	1.468578 (-7.7x10 ⁻⁴)	1.467817 (-2.6x10 ⁻⁴)
	20	1.469875	1.469991 (-7.9 x10 ⁻⁵)	1.470111 (-1.6x10 ⁻⁴)
633.2	25	1.467565	1.467686 (-8.2x10 ⁻⁵)	1.467861 (-2.0x10 ⁻⁴)
	30	1.465305	1.465381 (-5.2x10 ⁻⁴)	1.465616 (-2.1x10 ⁻⁴)
	20	1.468751	1.468244 (3.5x10 ⁻⁴)	1.469243 (-3.3x10 ⁻⁴)
657.2	25	1.466512	1.465938 (3.9x10 ⁻⁴)	1.466982 (-3.2x10 ⁻⁴)
	30	1.464256	1.463633 (4.3x10 ⁻⁴)	1.464696 (-3.0x10 ⁻⁴)

Table 4.12 Refractive index of $C_{12}H_{26}$ -THN (50 wt%) using Abbemat refractometer, correlation

Wave-	Mean				
wave-	Wiean	Experimental	Correlation	L-L mixing rule	
length	temperature	I		U	
		value	$(n_{experiment}-n_{correlation})$	$(n_{experiment}-n_{mixing rule})$	
(nm)	(\mathcal{L})				
436.1	20	1.528719	1.527048 (1.1x10 ⁻³)	1.531018 (-1.5x10 ⁻³)	
	25	1.526192	1.524593(1.0x10 ⁻³)	1.528419 (-1.5x10 ⁻³)	
	30	1.523667	1.522137 (1.0x10 ⁻³)	1.525809 (-1.4x10 ⁻³)	
	20	1.522668	1.522922 (-1.7x10 ⁻⁴)	1.522683 (-9.9x10 ⁻⁵)	
480.2	25	1.520243	1.520467 (-1.5x10 ⁻⁴)	1.520204 (2.6x10 ⁻⁵)	
	30	1.517776	1.518011 (-1.5x10 ⁻⁴)	1.517735 (2.7x10 ⁻⁵)	
546.3	20	1.515116	1.516737 (-1.1x10 ⁻³)	1.514935 (1.2x10 ⁻⁴)	
	25	1.512707	1.514282 (-1.0x10 ⁻³)	1.512493 (1.4x10 ⁻⁴)	
	30	1.510282	1.511826 (-1.0x10 ⁻³)	1.510044 (1.6x10 ⁻⁴)	
	20	1.511225	1.512714 (-9.9x10 ⁻⁴)	1.511346 (-8.0x10 ⁻⁵)	
589.3	25	1.508831	1.510258 (-9.5x10 ⁻⁴)	1.508934 (-6.8x10 ⁻⁵)	
	30	1.506367	1.507803 (-9.5x10 ⁻⁴)	1.506567 (-1.3x10 ⁻⁴)	
633.2	20	1.508312	1.508606 (-1.9x10 ⁻⁴)	1.508334 (-1.5x10 ⁻⁵)	
	25	1.505863	1.506150 (-1.9x10 ⁻⁴)	1.505931 (-4.5x10 ⁻⁵)	
	30	1.503377	1.503695 (-2.1x10 ⁻⁴)	1.503513 (-9.0x10 ⁻⁴)	
	20	1.506943	1.506360 (3.9x10 ⁻⁴)	1.507036 (-6.2x10 ⁻⁵)	
657.2	25	1.504502	1.503905 (4.0x10 ⁻⁴)	1.504642 (-9.3x10 ⁻⁴)	
	30	1.502100	1.501449 (4.3x10 ⁻⁴)	1.502222 (-8.1x10 ⁻⁴)	

Table 4.13 Refractive index of IBB-THN (50 wt%) using Abbemat refractometer, correlation

4.4 Summary

Results of temperature and concentration coefficients of refractive indices showed good agreement with the other optical methods [145; 146]. Refractive indices data for multiwavelength are scarcely available in literature. Exact value of refractive indices and its variation with temperature and concentration for different mixtures and wavelength have been measured using a multi-wavelength Abbemat refractometer. From all of the experiment, it has been found that temperature coefficient of refractive index is very small and does not change much with changing wavelength of the spectrum. However, concentration coefficient of refractive index strongly depends on molecular structure and most significance for the binary mixtures of alkane-THN. As compare to temperature coefficient of refractive indices, variation of concentration coefficient is more significant with wavelength of the spectrum. New correlations for measuring refractive index as a function of concentration, temperature and wavelength have been presented for selected five binary mixtures. Additional theoretical comparisons have been made using L-L mixing rule and found good agreement with experimental data. These measured data would be used in next chapter for measuring thermodiffusion coefficients using optical digital interferometry technique.

Chapter 5

Measurement of Soret coefficients

5.1 Designing of the Soret cell

In this current study, two different Soret cells of same internal dimension but different in geometries have been used. In Soret cell 1, the internal volume for liquid is 10 mm x 10 mm x 5 mm (length, width and height), the top and bottom copper blocks are flat in shape and do not have any extension along the enclosing liquid. Also, the cell is insulated rigidly with Teflon as shown in figure 5.1. During the experiment, it was found that temperature difference of 10 $^{\circ}$ K between top and bottom wall of the first Soret cell can be easily achieved without having strong convective flow inside the Soret cell. However, after having few experimental runs, the glass part of it was broken and a new Soret cell as shown in figure 5.2 having a new design was required. The second Soret cell consists of transparent lateral walls clamped between two identical copper blocks of dimensions 30 mm x 30 mm x 20 mm.

A transparent and optical quality Hellma quartz glass (part number: 690.269.QS) of external dimensions 30 mm x 30 mm x 30 mm has been used for enclosing the liquid. The copper blocks have an extension of 1 cm x 1 cm x 0.25 cm along the enclosing liquid, as shown in figure 5.3. So, the actual volume of the enclosing liquid is 10 mm x 10 mm x 5 mm, where 5 mm is the height between two copper blocks, as shown in figure 5.2. Four plastic screws have been used for clamping of copper blocks and glass part. Plastic screws are heat resistant which reduce chances of transferring heat by conduction between top and bottom copper blocks. To reduce heat dissipation from the lateral walls, the cell was covered with Teflon prior to use.



Top view



Side view





Figure 5.2 Soret cell 2: (a) copper plates, (b) optical quality quartz, (c) holes for filling the liquid, (s) screws, (o) O-ring to prevent leakage.



Figure 5.3 Extruded metallic part inside the liquid

In the current design of the cell, it is possible to compensate the small volume expansion during the experiment by allowing a small dead volume filled with saturated vapour inside the copper blocks as shown in figure 5.4. Dead volume is required to reduce the possibility of bubble formation during the variation of temperature especially for the space experiments where there is no scope of refilling the Soret cell.



(1) Copper part; (2) Copper screw; (3) Liquid

Figure 5.4 Sealing of the liquid and pressure compensation system inside the Soret cell

Although the experimental design of current study is similar to literature [93], some modifications have been done to reduce the effect of convection. The Soret cell used by Mialdun and Shevtsova [93] was a cubic shaped of 10 mm x 10 mm x 10 mm (length x width x height)

with aspect ratio 1 such that the cell height was the same as the length of the cell and the thickness of the lateral glass wall was 5 mm. The Soret cell that has been used in this study is 10 mm x 10 mm x 5 mm with aspect ratio 2 such that the cell height is the half of its length and the thickness of the lateral glass wall was 10 mm. Larger aspect ratio has reduced the effect of convection in the central portion of the cell and thicker lateral glass wall reduced the effect of environmental temperature on the fluid. In addition to reduce the chances of heat transfer between top and bottom copper blocks of the Soret cell, metallic screws have been replaced by plastic screws and to reduce lateral heat transfer during the experiment, Soret cell has been insulated by Teflon.

The thermal analysis and the geometrical design of the Soret cell 2 have been done using 2-D finite element CFD modelling of 120 by 120 mesh sizes. To observe enough separation of components between top and bottom wall, temperature difference (Δ T) was expected to increase as much as possible without having strong convective flow. However, as seen in figure 5.5(a), for applied Δ T of 10 °K, isotherms inside the cell show non-uniformity, because of the presence of convective cells as seen from figure 5.5(b).



Figure 5.5 2-D thermal modelling of the thermodiffusion cell: (C) Copper, (G) Glass and (L)

liquid

5.2 Calculation of Soret coefficients

Using the contrast factors $\left(\frac{\partial n}{\partial c}\right)_{T_0, c_0, \lambda}$ and $\left(\frac{\partial n}{\partial T}\right)_{T_0, c_0, \lambda}$ which are known from chapter 4, evolution of concentration and temperature in the 2D map as shown in figure 5.6 can be easily calculated from equation (3.17). Temperature inside the cell has been calculated from the images of first 3 to 5 minutes of thermodiffusion part. Any change of concentration during that time has been neglected. Temperature plot along the vertical median direction has been shown in figure 5.7. From figure 5.7, it is clear that the temperature inside the cell is almost linear and after three minutes temperature inside the cell become uniform as seen from both figure 5.7 and 5.8.



(a) 2-D Temperature distribution inside the diffusion cell



(b) 2-D concentration distribution inside the diffusion cell





Figure 5.7 Temperature plot along the vertical median direction



Figure 5.8 Transient temperature differences between top and bottom of the diffusion cell

Temperature difference does not change significantly after 5 minutes of applying thermal gradient, which is clear from figure 5.8. Temperature profiles show linearity for all mixtures,

which was desired not to have any disturbance due to the strong convective flow inside the diffusion cell. Transient evolution of concentration during the entire experiment has been shown in figure 5.9. The experimental data fit well with the analytical solution which will be discussed in section 5.4. Calculated concentration difference $\Delta c(x, y, t_{\infty})$ between top and bottom part of the diffusion cell at the steady state condition $(t = \infty)$ has been used to calculate the Soret coefficient, $S_{\rm T}$. The Soret coefficient $S_{\rm T}$ is the ratio of thermodiffusion coefficient $D_{\rm T}$ to the molecular diffusion coefficient $D_{\rm M}$. So,

$$S_T = \frac{D_T}{D_M}$$
(5.1)

If we re-call equation (1.3) which is

$$\Delta c(x, y, t_{\infty}) = -\frac{D_T}{D_M} c_0 (1 - c_0) \Delta T$$
(5.2)

By using equation (5.1), we can write

$$\Delta c_{st} \text{ or } \Delta c(x, y, t_{\infty}) = -S_T c_0 (1 - c_0) \Delta T$$
(5.3)

So, the Soret coefficient is

$$S_T = \frac{-1}{c_0(1-c_0)} \frac{\Delta c(x, y, t_\infty)}{\Delta T}$$
(5.4)

Details and step by step procedure of calculating Soret coefficients has been summarized in figure 5.10. For testing the accuracy of current image processing method, a comparison of image analysis for the same IVIDIL experiment of run 2 performed on board of ISS has been compared with literature [107] and shown in figure 5.11. From figure 5.11, it is clear that current image

analysis is correct and can be applied for the other experiment performed both in ground and on board of ISS.



Figure 5.9 Transient separation of THN in the mixture of $THN-C_{12}H_{26}$ between top and bottom

of the cell



Figure 5.10 Details steps of calculating Soret coefficient



Figure 5.11 Test of the current image processing methodology with literature

5.4 Calculation of Diffusion coefficients

To measure the Molecular diffusion coefficient, images of after changing the upper plate's temperature i.e. after eliminating temperature gradients are used. So, initially we have maximum concentration difference between top to bottom walls and this concentration gradient decreases slowly due to the molecular diffusion until reaching in to the homogeneous state. Using this interferometry technique, the concentration and temperature of any two dimensional point are calculated for the entire time period. Then, the calculated experimental concentration distribution is compared with the theoretical concentration distribution, which provides the diffusion coefficients. If we consider that there is no lateral heat transfer from the Soret cell, no convection and chemical reaction inside the Soret cell then separation of components due to the Soret effect would be purely diffusive. In addition, as the convection is negligible for this case, we can assume that both the temperature, T(x,y) and concentration c(x,y) can be considered as one dimensional i.e. vary along the vertical direction (y direction) only. So, the mass transport is caused by temperature and concentration gradient only. 1-D heat conservation equation is,

$$\rho c_p \frac{\partial T(y,t)}{\partial t} = -\vec{\nabla} J_T \tag{5.5}$$

And, 1-D mass conservation equation is

$$\rho \frac{\partial c(y,t)}{\partial t} = -\vec{\nabla} J_c \tag{5.6}$$

Where the heat flux,

$$\vec{J}_T = -\kappa \nabla T(y, t) \tag{5.7}$$

And the mass flux is,

$$\vec{J}_c = -\rho \Big[D_M \vec{\nabla} c(y,t) + D_T c_o (1 - c_o) \vec{\nabla} T(y,t) \Big]$$
(5.8)

The boundary conditions are:

- (a) No mass flux perpendicular to the impermeable wall i.e., $\vec{J}_c \cdot \vec{n} = 0$; where, \vec{n} is the normal vector,
- (b) The lateral walls are thermally insulated, and
- (c) The temperature of the top copper block is higher than the lower one.

In Cartesian co-ordinate system, if *y*-axis is assumed to be directed vertically from cold (y = 0) to hot wall (y = l). Then, both the temperature *T* and concentration *c* are function of vertical coordinate and time only. Hence, T = T(y, t) and c = c(y, t).

The temperature profile is linear across the cell from top to bottom. So,

$$\vec{\nabla}T(y,t) = \frac{\partial T(y,t)}{\partial y} = \frac{\Delta T}{l}$$
(5.9)

Hence, the equation (5.8) becomes,

$$\vec{J}_{c} = -\rho \left[D_{M} \vec{\nabla} c(y,t) + D_{T} c_{o} (1 - c_{o}) \frac{\Delta T}{l} \right]$$
(5.10)

Using equation (5.10), we can write equation (5.6) as

$$\frac{\partial c(y,t)}{\partial t} = D_M \frac{\partial^2 c(y,t)}{\partial y^2}$$
(5.11)

And from the boundary condition (a), we have $\vec{J}_c \cdot \vec{n} = 0$. So,

$$\vec{J}_{c} = -\rho \left[D_{M} \vec{\nabla} c(y,t) + D_{T} c_{o} (1 - c_{o}) \frac{\Delta T}{l} \right] = 0$$
(5.12)

By simplifying we get,

$$\vec{\nabla}c(y,t) = -\frac{D_T}{D_M}c_o(1-c_o)\frac{\Delta T}{l}$$
(5.13)

So, finally

$$\frac{\partial c(y,t)}{\partial y} = -S_T c_o (1 - c_o) \frac{\Delta T}{l}$$
(5.14)

where, S_T is the Soret coefficient. Using the above mentioned boundary conditions, the solution of equation (5.11) using variable of separation method is,

$$c(y,t) = c_o + S_T c_o (1 - c_o) \frac{\Delta T}{l} \left(\frac{l}{2} - y \right) + \left[S_T c_o (1 - c_o) \Delta T \sum_{n=1}^{\infty} \frac{2[(-1)^n - 1]}{n^2 \pi^2} \cos\left(\frac{n\pi y}{l}\right) \exp\left(-\frac{n^2 \pi^2 t D_M}{y}\right) \right]$$
(5.15)

Second term of right side of equation (5.15) is non zero only for odd values of n. So,

$$c(y,t) = c_o + S_T c_o (1 - c_o) \Delta T \left[\frac{1}{2} - \frac{y}{l} - \frac{4}{\pi^2} \sum_{n, odd} \frac{1}{n^2} \cos\left(\frac{n\pi y}{l}\right) \exp\left(-\frac{n^2 \pi^2 t D_M}{y}\right) \right]$$
(5.16)

Equation (5.16) represents the transient one dimensional distribution of component for the Soret separation part. As mentioned earlier, the experiment has two successive parts which are Soret separation part where concentration gradient builds up at the presence of temperature gradient and the pure diffusion part without presence of temperature gradient i.e.

$$\vec{\nabla}T(y,t) = \frac{\partial T(y,t)}{\partial y} = \frac{\Delta T}{l} = 0$$
. So, equation (5.15) can be written as,

$$c(y,t) = c_o + \left[S_T c_o (1-c_o) \Delta T \sum_{n=1}^{\infty} \frac{2\left[(-1)^n - 1 \right]}{n^2 \pi^2} \cos\left(\frac{n\pi y}{l}\right) \exp\left(-\frac{n^2 \pi^2 t D_M}{y}\right) \right]$$
(5.17)

Using equation (5.3) which is the steady state condition and only for odd values of n, we can rewrite equation (5.17) as,

$$c(y,t) = c_o - \Delta c_{st} \left[\frac{4}{\pi^2} \sum_{n,odd} \frac{1}{n^2} \cos\left(\frac{n\pi y}{l}\right) \exp\left(-\frac{n^2 \pi^2 t D_M}{y}\right) \right]$$
(5.18)

Soret coefficient S_T already calculated using equation (5.4), which can be applied in both equation (5.16) and (5.18) for calculating other unknown parameters i.e D_M . To find out D_M , the following cost function $f(D_M)$ has been applied:

$$f(D_M) = \sum_{y=1}^{l} \sum_{i=1}^{t} e_{y,i}^2$$
(5.19)

Where, *y* represents summation of all pixels in vertical direction of the Soret cell from 1 to *l* and i denotes the acquired images during the experiment. Here an important point to be noted that although the acquired images were two-dimensional, all images have been made one dimensional by taking the average values of all horizontal pixels.

5.5 Theoretical calculation of Soret and diffusion coefficients

Still now, the theory of calculating energy of viscous flow (ΔU_i^{visc}) is not well established and values of τ_i can be varied from 3 to 5. In this current study, it has been found that the calculated values of thermodifusion coefficients agree with experimental data for $\tau_1 = 4$ and τ_2 = 3. The physical parameters of the pure components used for the current study have been shown in table 5.1.

5.6 Results

The experimental results of Soret coefficients along with the theoretical calculation as discussed in section 1.5 have been summarized in table 4.3. The experimental results of IBB- $C_{12}H_{26}$ and THN-IBB show good agreement with the available literature (benchmark) values, but

shows difference for the mixture of THN-C₁₂H₂₆. The reason of not having close agreement for THN-C₁₂H₂₆ is that this mixture consists of Tetralin of double benzene structure and Dodecane of simple carbon chain; both are non-ideal in size and shape. So, the separation behaviour of this mixture would not be the same as other two mixtures. Moreover, the benchmark value of THN-C₁₂H₂₆ is composed of four different techniques and has large error bar i.e. ± 0.5 , so it is desired that results of other experimental technique may not agree with them. Based on our knowledge, there is no experimental data available for the mixtures of IBB-C₁₀H₂₂ and THN-C₁₀H₂₂ are close to validate our results. However, Soret coefficient of IBB-C₁₀H₂₂ and THN-C₁₀H₂₂ are close to IBB-C₁₂H₂₆ and THN-C₁₂H₂₆. The reason of similarity of the Soret coefficients values is that both Decane (C₁₀H₂₂) and Dodecane (C₁₂H₂₆) are similar in atomic structure, only difference of just two carbon atoms.

Table 5.1 Physical properties of pure components used for PR-EOS at $T_0 = 298$ °K, Pressure = 1

							Liquid	
Component	Acentric factor	Critical temperature (°K)	Critical pressure (10 ⁶ Pa)	Molecular weight (g.mol ⁻¹)	Critical volume (x10 ⁻³ m ³ .kg ⁻¹)	Viscosity (cp)	volume at boiling temperature (cm ³ .mol ⁻¹)	Shift parameter
$C_{10}H_{22}$	0.4842	618.45	2.123	142.285	4.239	0.8718	235.52	0
$C_{12}H_{26}$	0.5734	658.2	1.8239	170.338	4.267	1.09068	287.249	0.11498
IBB	0.3811	650.15	3.0398	134.22	3.397	0.9998	187.48	0
THN	0.3278	720.15	3.62	132.205	3.336	2.010	163.329	0.0146

atm

		IBB-	THN-	IBB-	THN-	
Contributor	Quantity	$C_{10}H_{22}$	$C_{10}H_{22}$	$C_{12}H_{26}$	$C_{12}H_{26}$	THN-IBB
	D_M ; $10^{-10} m^2 s^{-1}$	-	-	9.5±0.4	6.21±0.06	8.5±0.6
Ref. [152]	D_{T} ; $10^{-12} m^{2}s^{-1}$	-	-	3.7±0.2	5.9±0.3	2.8±0.1
	S_{T} ; 10 ⁻³ K ⁻¹	-	-	3.9±0.1	9.5±0.5	3.3±0.3
	$D_{\rm M}; 10^{-10} {\rm m}^2 {\rm s}^{-1}$	-	-	9.62±0.25	6.22±0.09	7.71±0.34
Ref. [60]	D_{T} ; $10^{-12} \text{ m}^{2}\text{s}^{-1}$	-	-	3.88±0.13	6.00±0.13	2.80±0.24
	S_{T} ; 10 ⁻³ K ⁻¹	-	-	4.03±0.09	9.65±0.16	3.63±0.27
Dof [72]	$D_{\rm M}; 10^{-10} {\rm m}^2 {\rm s}^{-1}$	-	-	9.32±0.12	6.27±0.29	8.52±0.12
Rel. [75]	S_{T} ; 10 ⁻³ K ⁻¹	-	-	3.98±0.008	9.24±0.01	3.29±0.11
Current Study,	$D_{\rm M}; 10^{-10} {\rm m}^2 {\rm s}^{-1}$	-	-	9.54±0.3	5.97±0.8	8.43±0.14
experiment ^a	S_{T} ; 10 ⁻³ K ⁻¹	-	-	3.70±0.05	8.56±0.11	3.16±0.06
Current Study,	$D_{\rm M}; 10^{-10} {\rm m}^2 {\rm s}^{-1}$	5.21±0.24	5.97±0.64	9.57±0.34	6.02±0.4	8.37±0.22
experiment ^b	S_{T} ; 10 ⁻³ K ⁻¹	4.13±0.18	8.23±0.17	3.93±0.19	8.62±0.18	3.25±0.22
Current Study,	$D_{\rm M}; 10^{-10} {\rm m}^2 {\rm s}^{-1}$	11.08	6.84	9.52	10.8	4.86
theoretical	S_{T} ; 10 ⁻³ K ⁻¹	3.07	7.31	3.64	9.40	2.32

Table 5.2 Measured values and comparison with literature at mass fraction of 0.50 and

temperature of 25 °C

^aUsing Soret cell 1 of without extruding metallic part, applied $\Delta T = 10$ ^oK

^bUsing Soret cell 2 of with extruding metallic part, applied $\Delta T = 2$ ^oK

The theoretical model was not able to predict the diffusion coefficients very well especially for the mixtures of $IBB-C_{10}H_{22}$ and THN-IBB, which can be improved to fit with the
experimental results by changing the values of τ_i . However, at the end, the theoretical results are just calculated values and will not provide anything new unless the theory of calculating energy of viscous flow has been established.

5.7 Summary

In this current study, optical digital interferometry technique using Mach-Zehnder Interferometer has been built up and used for measuring the Soret coefficients. One of the preliminary purposes was to test the experimental set up as well as the thermal design of Soret cell. Experimental results showed maximum deviation of less than 2% for two mixtures and 9% for the third mixture from the benchmark data [152]. The reason of deviation of the experimental data comes from the variation of techniques and the external noises due to the change of temperature of the experimental condition over time, but not from the experimental method. The experimental set up can be improved further by redesigning the Soret cell 2 to apply higher ΔT such as 10 °K or even more, which was the case for the Soret cell 1. Whole experimental setup was isolated by using plastic foam insulator to avoid any disturbances coming from the external light source as well as changing the temperature during the running period of the experiment.

Chapter 6

Error Analysis

6.1 Introduction

No matter how carefully an experiment is performed, errors always present in the experiment. There are two types of experimental errors namely systematic error and random error. Systematic error is related to the apparatus and cannot be improved by repeated the experiment. Common systematic errors in MZI techniques are stability of laser wavelength, resolution of the electronics component etc. Random error is related to the variation of the same measurement while repeating the experiment. Electronics components also produce random error by providing different values in the repeated experiment. Major random error of MZI is caused by the environment such as variation of air temperature, humidity etcetera.

6.2 Sources of error in MZI

6.2.1 Geometric errors

Geometric errors consist of alignment error, target uniformity and Abbe' error. This error can be reduced by using rigid set-up, proper alignment and using optically flat mirrors. Alignment error comes from the angular misalignment between the measurement (vertical) axis and the axis of the laser beam. Target uniformity represents the error caused by surface roughness of the mirror, which is the largest geometrical error. Abbe' error comes from the offset between the measurement axis and the laser beam axis. To reduce the alignment error, overlap between the target and reference beam must be close to 100%. Misalignment of the measurement beam to the measurement plane was visualized by observing overlapping of the two beams at the beam splitter where two beams re-combine and far from the beam splitter. For example: 1 mm run out at a distance of 1 m from the beam splitter yields alignment error of 1 mm/ 1m which is equal to 1 mrad.

A mirror with a surface roughness of $\lambda/10$ can contribute up to 632.8/10 or 63.28 nm of error. Opposite axis error is the mechanical error caused when perpendicular axes are not exactly orthogonal to each other. Mechanical stability depends on the mounting stiffness and the vibration. In the current study, geometric errors have been avoided by subtracting all images from the reference image and mounting all equipments rigidly to the optical table.

6.2.2 Instrumental errors

Instrumental errors are based on the supplier's system parameters and are not under control of users. These errors come from wavelength of the laser source, electronics, interferometer etc. When working with a laser, it is very important to know the exact wavelength the laser is producing. Most of the manufacturers provide accuracy of laser wavelength in terms of ppm. If manufacturing company mentions ± 1 ppm tolerance, the actual wavelength of a laser of 1000 nm wavelength is 1000 ± 0.001 nm. The red He-Ne laser is always 632.8 nm, because it is defined to within a small fraction of a nanometer. However, when working with a tunable wavelength laser or a laser that can experience significant wavelength drift as a function of temperature or time, it is important to know the stability characteristics.

6.2.3 Environmental errors

Environmental errors are the largest error in MZI. Variation of refractive index of the air changes the wavelength of the laser source and changes the length of the optical path. This change is caused by the temperature, pressure and humidity of air. Controlling environment and if possible reducing the measurement time reduce the environmentally induced errors. To compensate for the changes in the air temperature, pressure and humidity, the vacuum wavelength of the measurement beam, λ_{vac} is divided by the index of refraction of air, n_{air} . Air turbulence is the movement of thermal gradients in the air through the beam path. It can be reduced by placing tubes along the beam path. It can be done more preciously by operating the experiment in Helium filled or vacuum atmosphere.

As mentioned earlier, Interferometry techniques are popular due to the non-intrusiveness and good accuracy without any calibration. However, one of the major disadvantages is that some minor external effects influence the entire experiment, for example the variation of external temperature. To test the effect of the environmental temperature, images have been grabbed for both short term such as 2 hours and long term such as 20 hours as shown in figure 6.1. Typically, the duration of the experiment is between 8 to 12 hours, so the long term sensitivity test is enough for judging the overall sensitivity of the experiment. The calculated standard deviation for short term test has been found to be 0.1117 radian, while for the long term test the standard deviation is 0.1052 radian. From figure 3.3, we can see that the maximum phase evolution is between 40 to 50 radians. So, the possible error due to the change of environmental temperature is less than 0.2%.



Figure 6.1 Sensitivity of the MZI

6.3 Error analysis

In this current study, only phase shift from the initial condition has been used for calculating temperature and concentration coefficients of refractive indices as well as transport coefficients. So, some of the geometrical and instrumental errors are cancelled out. However, there are some other types of errors that affect the experiment. In this chapter, detail error analysis has been performed.

6.3.1 Errors in refractive index measurement

Optical path variation of laser beam is linked to the phase variation $(\Delta \varphi)$ as,

$$\Delta p = \frac{\Delta \varphi \lambda}{2\pi} \tag{6.1}$$

Where, λ is wavelength of the laser. The refractive index change (Δn) is related with path variation as,

$$\Delta p = \Delta n.l \tag{6.2}$$

Where, l is the optical thickness. By using equation (6.1), we can re-write the related refractive change as,

$$\Delta n = \frac{\Delta \varphi \lambda}{2\pi l} \tag{6.3}$$

So, the Root Sum Square (RSS) accuracy of refractive index variation is, $\delta(\Delta n) = sqrt \left[\left\{ \frac{\lambda}{2\pi l} \cdot \delta(\Delta \varphi) \right\}^2 + \left\{ \frac{\Delta \varphi \cdot \lambda}{2\pi} \cdot \left(\frac{-1}{l^2} \right) \cdot \delta(l) \right\}^2 + \left\{ \frac{\Delta \varphi}{2\pi l} \cdot \delta(\lambda) \right\}^2 \right]$ (6.4)

Equation (6.4) can be used for calculating the accuracy of temperature and concentration coefficient of refractive index as well as transport coefficients.

6.3.2 Errors in coefficients of refractive index

6.3.2.1 For MZI technique

Temperature coefficient of refractive index is related with refractive index and temperature,

$$\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda} = \frac{\Delta n_T}{\Delta T} \tag{6.5}$$

So, the RSS error associated with measurement of temperature coefficient of refractive index is related with the measurement error of refractive index and temperature as,

So,
$$\delta \left(\frac{\partial n}{\partial T}\right)_{c_0, \lambda} = sqrt \left[\left\{ \frac{1}{\Delta T} \cdot \delta(\Delta n_T) \right\}^2 + \left\{ \Delta n_T \cdot \left(\frac{-1}{\Delta T^2}\right) \cdot \delta(\Delta T) \right\}^2 \right]$$
 (6.6)

Similarly,

So,
$$\delta \left(\frac{\partial n}{\partial c}\right)_{c_0,\lambda} = sqrt \left[\left\{ \frac{1}{\Delta c} \cdot \delta(\Delta n_c) \right\}^2 + \left\{ \Delta n_c \cdot \left(\frac{-1}{\Delta c^2}\right) \cdot \delta(\Delta c) \right\}^2 \right]$$
 (6.7)

The accuracy of temperature measurement using Peltier is ± 0.01 °K. For measuring $\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$,

temperature range of 296 °K to 300 °K ($\Delta T = 4$ °K) has been used. And, for measuring $\left(\frac{\partial n}{\partial c}\right)_{c_0, \lambda}$,

concentration or mass fraction difference 0.0042 has been used. The accuracy of measurement of mass is 5 ± 0.001 gm. So, the accuracy of mass fraction, $\delta(\Delta c)$ is $0.001/5 = 2x10^{-4}$. The calculated accuracy of individual mixtures and the values used for the calculation is shown in table 6.1.

Mixtures	ΔT; °K	δ(ΔT); °K	Δn_T x10 ⁻³	$\delta(\Delta n_T)$ x10 ⁻⁶	$\delta \left(\frac{\partial n}{\partial T} \right)_{c_0, \lambda}$ $x 10^{-6}; K^{-1}$	Δc	$\delta(\Delta c)$ x10 ⁻⁴	Δn _c x10 ⁻⁴	δ(Δn _c) x10 ⁻⁶	$\delta \left(\frac{\partial n}{\partial c}\right)_{c_0, \lambda}$ $x 10^{-3}, K^{-1}$
C ₁₂ H ₂₆ - IBB	4	±0.01	1.41	8.68	2.34	0.0 042	2	2.56	5.25	3.3
С ₁₂ Н ₂₆ - ТНN	4	±0.01	1.34	8.43	2.27	0.0 042	2	4.82	5.69	5.6
IBB-THN	4	±0.01	1.41	8.64	2.35	0.0 042	2	2.21	5.33	2.8

Table 6.1. Accuracy of measuring coefficients of refractive indices using MZI

At the time of measuring temperature coefficient of refractive index, it is also important to consider the change of refractive index of the glass part (optical window) due to the temperature variation as well as the change of the optical path length due to thermal expansion of the glass part. The error caused by the temperature distribution inside the glass can be express as [153],

$$e_{g} = \left(n_{g} - n_{\infty}\right)\beta_{g} + \frac{\partial\left(n_{g} - n_{\infty}\right)}{\partial T}$$
(6.8)

Where, n_g is the refractive index of glass, n_∞ is the refractive index of air, β_g is the thermal expansion coefficient and T is the temperature. The glass part used in the current study is Heraeus Quartz glass. Which has the properties [154]: $n_g = 1.45702$; $n_\infty = 1$; mean thermal expansion coefficient at temperature range of 0 to 100 °C, $\beta_g = 5.1 \times 10^{-7}$ K⁻¹; Temperature coefficient of refractive index relative to air, $\frac{\partial (n_g - n_\infty)}{\partial T} = 9.839 \times 10^{-6}$ K⁻¹ at wavelength $\lambda = 632.8$ nm. So, the calculated value of e_g of equation (6.8) is 1.01×10^{-5} K⁻¹ at wavelength of 632.8 nm.

Therefore, the error caused by the wavefront distortion generation due to the inhomogeneous thermal expansion of the glass and refractive index change of the glass with temperature is small but non-zero. Thermal expansion coefficient of all type of glasses is positive, but temperature coefficient of the glass can be positive or negative. Hence, the error can be made zero by choosing 'athermal' glass. Athermal glass has the negative temperature coefficient of refractive index and positive thermal expansion coefficient. So, the numerical value of $e_{\rm g}$ can be zero.

6.3.2.2 Error analysis for Abbemat refractometer

Temperature coefficient of refractive index is related with refractive index temperature,

$$\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda} = \frac{\Delta n_T}{\Delta T}$$
(6.9)

So, the error associated with measurement of temperature coefficient of refractive index is related with the measurement error of refractive index and temperature as,

So,
$$\delta \left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda} = sqrt \left[\left\{ \frac{1}{\Delta T} \cdot \delta(\Delta n_T) \right\}^2 + \left\{ \Delta n_T \cdot \left(\frac{-1}{\Delta T^2}\right) \cdot \delta(\Delta T) \right\}^2 \right]$$
 (6.10)

Manufacturer defined accuracy of measuring refractive index, $\delta(\Delta n)$ of the Abbemat refractometer is $\pm 4 \times 10^{-5}$ and the accuracy of temperature measurement is also defined as ± 0.03 ^oK [148]. Similarly, the accuracy of measuring concentration coefficient of refractive index is,

So,
$$\delta \left(\frac{\partial n}{\partial c}\right)_{c_0, \lambda} = sqrt \left[\left\{ \frac{1}{\Delta c} \cdot \delta(\Delta n_c) \right\}^2 + \left\{ \Delta n_c \cdot \left(\frac{-1}{\Delta c^2}\right) \cdot \delta(\Delta c) \right\}^2 \right]$$
 (6.11)

The accuracy of measurement of mass is 5 ± 0.001 gm. So, the accuracy of mass fraction is $0.001/5 = 2 \times 10^{-4}$. Details of the calculated values have been summarized in table 6.2.

5.3.3 Error calculations of transport coefficient

The accuracy of measuring refractive index is directly related to the measurement of temperature and concentration coefficients of refractive indices using MZI and for measurement of transport coefficients. In the current study, two lasers of wavelength 632.9 nm and 639 nm have been used. Table 6.3 shows the calculated accuracy for individual mixtures as well as different lasers.

Mixtures	ΔΤ; °K	δ(ΔT); °K	Δn_T 10^{-3}	$\delta(\Delta n_T)$ 10^{-5}	$\delta \left(\frac{\partial n}{\partial T}\right)_{c_0, \lambda} 10^{-6}; \mathrm{K}^{-1}$	Δc	δ(Δc) 10 ⁻⁴	Δn_c 10^{-3}	$\delta(\Delta n_c)$ 10^{-5}	$\delta \left(\frac{\partial n}{\partial c}\right)_{c_0, \lambda}$ 10^{-4}
C ₁₀ H ₂₂ - IBB	12	±0.03	5.76	±4	3.54	0.08	2	5.52	±4	5.30
C ₁₀ H ₂₂ - THN	12	±0.03	5.63	±4	3.54	0.08	2	8.98	±4	5.73
C ₁₂ H ₂₆ - IBB	11	±0.03	5.23	±4	3.86	0.08	2	5.34	±4	5.27
C ₁₂ H ₂₆ - THN	12	±0.03	5.54	±4	3.53	0.08	2	8.77	±4	5.70
IBB-THN	12	±0.03	6.01	±4	3.56	0.08	2	4.06	±4	5.16

Table 6.2 Accuracy of measuring coefficients of refractive indices using Abbemat refractometer

Table 6.3 Accuracy of measuring refractive indices for transport coefficients

Mixtures	λ; nm	$\delta(\lambda);$ nm	<i>l</i> ; m	δ(<i>l</i>); m	$\Delta arphi$; rad	$\delta(\Delta \varphi);$ rad	$\delta(\Delta n) \ 10^{-4}$
C ₁₀ H ₂₂ -IBB	632.9	±0.1	0.01	±5x10 ⁻⁵	12.39	±0.5	1.25
C ₁₀ H ₂₂ -THN	632.9	±0.1	0.01	±5x10 ⁻⁵	41.07	±0.5	4.14
C ₁₂ H ₂₆ -IBB	639	±0.1	0.01	±5x10 ⁻⁵	31.42	±0.5	3.20
C ₁₂ H ₂₆ -IBB	632.9	±0.1	0.01	$\pm 5 \times 10^{-5}$	10.93	±0.5	1.10
C ₁₂ H ₂₆ -THN	639	±0.1	0.01	$\pm 5 \times 10^{-5}$	56.55	±0.5	5.75
C ₁₂ H ₂₆ -THN	632.9	±0.1	0.01	$\pm 5 \times 10^{-5}$	41.60	±0.5	4.19
IBB-THN	639	±0.1	0.01	$\pm 5 \times 10^{-5}$	25.13	±0.5	2.56
IBB-THN	632.9	±0.1	0.01	$\pm 5 \times 10^{-5}$	7.66	±0.5	0.77

Measurement of temperature from the thermodiffusion experiment is related to the change of refractive index as,

$$\Delta T = \frac{\Delta n}{\left(\frac{\partial n}{\partial T}\right)_{c_0,\,\lambda}} \tag{6.12}$$

So, the accuracy of temperature measurement is,

$$\delta(\Delta T) = sqrt\left[\left\{\frac{1}{\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}}.\delta(\Delta n)\right\}^2 + \left\{\Delta n \left(\frac{-1}{\left\langle\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}\right\rangle^2}\right).\delta\left\langle\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}\right\rangle\right\}^2\right]$$
(6.13)

Similarly, the accuracy of concentration measurement is,

$$\delta(\Delta c) = sqrt\left[\left\{\frac{1}{\left(\frac{\partial n}{\partial c}\right)_{c_{0},\lambda}}.\delta(\Delta n)\right\}^{2} + \left\{\Delta n.\left(\frac{-1}{\left\langle\left(\frac{\partial n}{\partial c}\right)_{c_{0},\lambda}\right\rangle^{2}}\right).\delta\left\langle\left(\frac{\partial n}{\partial c}\right)_{c_{0},\lambda}\right\rangle\right\}^{2}\right]$$
(6.14)

The Soret coefficient is related with change of concentration at steady state condition and change of temperature

$$S_T = \frac{-1}{c_0 (1 - c_0)} \frac{\Delta c}{\Delta T} \tag{6.15}$$

In this current study mass fraction 50% such that $c_0 = 1-c_0$. So,

$$S_T = \frac{-1}{c_0^2} \frac{\Delta c}{\Delta T} \tag{6.16}$$

So, the accuracy of measurement of S_T is,

$$\delta(S_T) = sqrt\left[\left\{\frac{-1}{c_0^2} \cdot \frac{1}{\Delta T} \cdot \delta(\Delta c)\right\}^2 + \left\{\frac{-\Delta c}{\Delta T} \cdot \frac{-2}{c_0^3} \cdot \delta(c_0)\right\}^2 + \left\{\frac{-\Delta c}{c_0^2} \cdot \frac{-1}{\Delta T^2} \cdot \delta(\Delta T)\right\}^2\right]$$
(6.17)

Detail calculated error values have been summarized in table 6.4.

Mixtures	$\left(\frac{\partial n}{\partial T}\right)_{c_0,\lambda}$ $x10^{-4},\mathrm{K}^{-1}$	$\delta \left(\frac{\partial n}{\partial T}\right)_{c_0, \lambda}$ $x 10^{-6}, K^{-1}$	δ(ΔT); °K	$\left(\frac{\partial n}{\partial c}\right)_{c_0,\lambda}$	$\delta \left(\frac{\partial n}{\partial c}\right)_{c_0,\lambda} x 10^{-4}$	$\delta(\Delta c)$ x10 ⁻⁵	$\delta(S_T)$ x10 ⁻⁴
^b C ₁₀ H ₂₂ -IBB	-4.79	3.54	0.018	-0.0695	5.30	7.68	1.82
^b C ₁₀ H ₂₂ -THN	-4.71	3.54	0.018	-0.1156	5.73	6.42	1.72
^a C ₁₂ H ₂₆ -IBB	-4.42	2.34	0.020	-0.0625	33.0	9.75	0.50
^b C ₁₂ H ₂₆ -IBB	-4.75	3.86	0.019	-0.0644	5.27	8.24	1.94
^a C ₁₂ H ₂₆ -THN	-4.29	2.27	0.020	-0.1148	56.0	21.5	1.13
^b C ₁₂ H ₂₆ -THN	-4.60	3.53	0.019	-0.1118	5.70	6.57	1.79
^a IBB-THN	-4.70	2.35	0.018	-0.0525	28.0	10.6	0.55
^b IBB-THN	-4.98	3.56	0.017	-0.0546	5.16	9.65	2.24

Table 6.4 Accuracy of measuring transport coefficients

^aUsing Soret cell 1 of without extruding metallic part, applied $\Delta T = 10$ °K

^bUsing Soret cell 2 of with extruding metallic part, applied $\Delta T = 2$ ^oK

6.4 Summary

Uncompensated system provides error associated with refractive index. In this chapter all types of possible error sources have been identified and calculated. Complete measurement of uncertainty has been done to know the capability of the MZI and Abbemat refractometer. There is additional error presented in the experiments of this current study due to the presence of impurities in the fluid material. The fluid materials are more than 98% pure, the information about rest of the 2% components are unknown. Maximum error of measuring Soret coefficients has been found 2.24×10^{-4} or less than 0.022%.

Chapter 7

Conclusions, contributions and future recommendations

7.1 Conclusion

Though, Soret coefficient of liquid mixtures is very small in magnitude, it is very important in many natural phenomenon as well as industrial applications. It has to be measured with high accuracy having minimum experimental errors. Measurement of Soret coefficient in terrestrial condition is very difficult due to the possibility of convective flow in the system. In this work a nonintrusive laser based optical method has been built and used to have smaller experimental errors. At the beginning, Soret coefficients of benchmark mixtures have been measured using two different Soret cell and compared with literature values for testing sensitivity of the experimental method and set up. Results show good agreement for two mixtures and slight difference for the third mixture. Later on, experiment has been expanded towards two more binary mixtures. Theoretical calculations of Soret coefficients has been done using nonequilibrium thermodynamic model and found good agreement with experimental value for τ_i values of 4 and 3.

Thermal design of the Soret cell has been performed to reduce convective flow and beam deflection problem has been solved by focusing the CCD camera on the liquid sample. Image analysis has been revised and updated to increase the accuracy of the results. Possible sources of other errors such as variation of external temperature during running the experiment, re-design of the Soret cell to have higher temperature gradient have been indentified and recommended for future research.

Laser based optical methods work based on the principle of variation of refractive index with temperature, concentration, pressure, wavelength etcetera. However, simple mathematical correlations to calculate refractive indices as a function of temperature, concentration and wavelength are necessary for optical based scientific researches. So, temperature and concentration coefficients of refractive indices have been measured in atmospheric pressure using both interferometer and Abbemat refractometer. New correlations of refractive indices as a function of temperature, concentration and wavelength have been provided. Actual values of refractive indices of pure and binary mixtures have been presented, which may be used by other scientific scholars.

For complete understanding of thermodiffusion effect and works done by our predecessors, a details historical literature survey has been done on both of the experimental works and theoretical models based on nonequilibrium thermodynamics. Other researchers will be highly benefitted from the literature survey.

All of the systematic and random errors have been identified and calculated. After completing error analysis, it has been shown clear that the capability of MZI is very good for measuring transport coefficients.

7.2 Contributions

The main objective of this current research was to build a laser based optical set up and to measure the thermodiffusion coefficients experimentally. A brand new experimental set up based on Mach-Zehnder interferometer (MZI) has been built in microgravity research lab, Ryerson University. Image processing methods has been built using some simple Matlab codes as shown in appendix A.3. Correlation of refractive indices has been measured and published partially in

different international conferences and completely in journal of optics and laser in engineering [155]. Results with detail experimental methods have been published in the journal of experimental thermal and fluid science [156]. Literature survey of both experimental and theoretical works and error analysis is under preparation for possible publications.

7.3 Future work

Although, in this current study diffusion coefficients have been measured successfully, there are still few limitations such as temperature of the entire set up was not regulated, current geometry of the Soret cell is not applicable for higher temperature gradient and all of the experiments were performed only for binary mixtures. Therefore, next step of this research would be further improvement of the set up by isolating and regulating the temperature and humidity of the whole set up using an air to air temperature cooler. Also, Soret cell can be upgraded having better cell geometry such as higher aspect ratio, upgrading the filling method of the liquid to avoid possibility of dissolved air etc. The set up can be used to measure Soret coefficient of ternary mixtures by simply adding one more extra laser diode. However, prior to use the set-up for ternary mixtures which is much complicated and required higher accuracy of the measurement, issues as discussed earlier must be solved.

Appendix

A.1: Multiple regressions analysis (MLR) using 'Microsoft excel data analysis' for C₁₀H₂₂-

THN

SUMMARY OUTPUT

Regression Statistic	°S	-			
Multiple R	0.9880	-			
R Square	0.9762				
Adjusted R					
Square	0.9754				
Standard Error	0.0012				
Observations	90				
ANOVA		-			
					Significance
	df	SS	MS	F	F
Regression	3	0.0047	0.001567	1177.857	$1.07 \text{x} 10^{-69}$
Residual	86	0.0001147	1.3281x10 ⁻⁶		
Total	89	0.00487			
		Standard			
	Coefficients	Error	t Stat	P-value	Lower 95%
Intercept	1.5832187	0.00243	651.1567	1.4×10^{-160}	1.578
Concentration of					
$C_{10}H_{22}$	-0.12051	0.0043	-28.059	4.66x10 ⁻⁴⁵	-0.129
Temperature	-0.000469	2.975x10 ⁻⁵	-15.767	4.21x10 ⁻²⁷	-0.00053
Wavelength	-7.677x10 ⁻⁵	1.5362x10 ⁻⁶	-49.976	2.5x10 ⁻⁶⁵	-8x10 ⁻⁵

Upper

95%

1.588

-0.112

-0.00041

-7.4x10⁻⁵

A.1.1 Explanation of results:

A.1.1.1 Regression Statistics:

1.1 R Square = $(Multiple R)^2 = R^2 = 1$ - Residual SS / Total SS = Regress SS / Total SS. It is the fraction of the variation in refractive index 'n' that is explained by equations in table 5, column 2. Where, SS means 'sum of squares'.

1.2 R = correlation coefficient.

1.3 Adjusted R Square = 1 - (Total df / Residual df)(Residual SS / Total SS). Where, df = degree of freedom.

1.4 Standard Error = (Residual MS) $^{0.5}$. Where, MS means 'Mean square' and MS = SS/df.

A.1.1.2 ANOVA (Analysis-of-variance):

2.1 Regression df = regression degrees of freedom = number of independent variables, which is 3 (concentration, temperature and wavelength) in this current study.

2.2 Regression SS = Total SS - Residual SS.

2.3 Regression MS = Regression SS / Regression df.

2.4 Regression F = Regression MS / Residual MS.

2.5 Significance $F = F_{distribution}$ (Regression F, Regression df, Residual df) = Probability that equations of table 5, column 2 do not explain the variation in refractive index 'n'. This is based on the F (Fisher) probability distribution. If the Significance F is not less than 0.10 (10%), there is no meaningful correlation. 2.6 Residual df = residual degrees of freedom = Total df - Regression df = N - 1 - number of independent variables. Where, N is the total number of observations.

2.7 Residual SS = sum of squares of the differences between the values of 'n' predicted by equations of table 5, column 2 and the actual values of 'n' measured by the experiment.

2.8 Residual MS = mean square error = Residual SS / Residual df.

2.9 Total df = total degrees of freedom = N - 1

2.10 Total SS = the sum of the squares of the differences between values of 'n' and the average 'n' = $(N-1) \times (\text{standard deviation of y})^2$.

2.11 Coefficients = values of coefficients which minimize the Residual SS (maximize R^2).

2.12 Standard error = (Residual MS using only the Coefficient for that row)^{0.5}.

2.13 t Stat = Coefficient for that variable / Standard error for that variable

2.14 P-value = the Student's t-distribution two-tailed probability. This probability needs to be small, certainly less than 0.10 (10%) in order to be sure that this variable really influences n. In the current study, all of the P values are much less than 0.10.

2.15 This is a 95% probability that the true value of the coefficient lies between the Lower 95% and Upper 95% values. The probability is 2.5% that it lies below the lower value, and 2.5% that it lies above. The narrower this ranges the better are the correlations.

A.2 Predicting mass fraction to measure concentration coefficient of refractive indices

Initial condition

Mass = 2.5 gm

Mass fraction of 1^{st} component = 0.0075 (pre-set)

So, mass fraction of 2^{nd} component = 1-0.0075 = 0.9925

So, $w_{1i} = 2.5*0.0075 = 0.01875$ gm

 $w_{2i} = 2.5*0.9925 = 2.48125 \ gm$

Added condition

Approximate Mass = 0.5 gm

Mass fraction of the 2 components = ? (**Required**)

Final condition

Mass = 2.5 + 0.5 = 3.0 gm

Mass fraction of 1^{st} component = 0.0225 (pre-set)

So, mass fraction of 2^{nd} component = 1-0.0225 = 0.9775

So, $w_{1i} = 3*0.0225 = 0.0675$ gm

 $w_{2i} = 3*0.9775 {=}\ 2.9325\ gm$

So, $w_{1added} = 0.0675 - 0.01875 = 0.04875$ gm

 $W_{2added} = 3.0-0.04875=0.45125 \text{ gm}$

So the mass fraction of component 1 of added solution is = 0.04875/3.0 = 0.04875/0.5 = 0.0975.

A.3 Matlab codes

A.3.1 Calculation of temperature and concentration from phase images

function temperature_concentration_plot

clc;

clear all;

close all;

- tth = 6; % thermal time
- td = 240; % number of images with dT=non-zero
- tend = 480; % total number of images
- dndT=-0.0004682; % temperature coefficient of refractive index
- lambda=639*1e-9; %wavelength of laser

depth=0.01; %optical depth

dndC= -0.06125; % concentration coefficient of refractive index

centralpixel=262/2;

w1m=0.5; % mean concentration

Tm=298; % mean temperature

%unplotted distance from bottom/cold wall

z1=(30*0.005/322)+(0.5*0.005/322);

%unplotted distance from top/hot wall

```
z2=0.005-(30*0.005/322)-(0.5*0.005/322);
```

L=linspace(z1,z2,261);

%step 1 from beginning to until temperature reach in steady state condition

for cpt=2:1:tth

```
n1='phase_ini-phase';
```

n2 = num2str(cpt);

while length(n2) < 4

n2 = ['0' n2];

end

n3='.txt';

nametot=[n1 n2 n3];

%name1=sprintf('phase_ini-phase%d.txt',cpt);

```
name1=nametot;
```

```
UPhi1=dlmread(name1);
```

```
UPhi1mean1=mean(UPhi1);
```

```
n(cpt,:)=UPhi1mean1*lambda/(2*pi*depth); % calculation of refractive indices from
```

phase

T(cpt,:)=(n(cpt,:)/(dndT)); %calculation of temperature from phase

```
T(cpt,:)=T(cpt,:)-T(cpt,centralpixel)+Tm;
```

dT(cpt) = T(cpt,end-10)-T(cpt,10);

dT(cpt) = abs(dT(cpt)); % calculation of temperature difference between top and

bottom wall

```
fid=fopen('DelT.txt','A');
```

```
fprintf(fid,'%6E',dT(cpt));
```

fprintf(fid,'\r\n');

fclose(fid)

end

figure

```
plot(L,T(2,:),'r',L,T(tth-2,:),'g',L,T(tth,:),'k') %temperature plot along vertical direction
```

title('Temperature plot upto thermal time')

xlabel('Length (m)')

ylabel('Temperature (Kelvin)')

figure

%plot(t1,dT,'y')

plot(dT,'r')

title('Temperature difference Vs time upto thermal time')

xlabel('Time (minute)')

```
ylabel('Delta T (Kelvin)')
```

%step 2 after temperature reaches in steady state to maximum Soret separation i.e. concentration

reaches in steady state condition

for cpt=tth+1:1:td

```
n1='phase_ini-phase';
```

n2 = num2str(cpt);

while length(n2)<4

```
n2 = ['0' n2];
```

end

n3='.txt';

```
nametot=[n1 n2 n3];
```

```
name2=nametot;
```

```
UPhi2=dlmread(name2);
```

```
UPhi1mean2=mean(UPhi2);
```

```
n(cpt,:)=UPhi1mean2*lambda/(2*pi*depth); %calculation of refractive indices from
```

phase

```
w1e(cpt,:)=(n(cpt,:)-n(tth,:))/dndC; %calculation of concentration from phase
w1e(cpt,:)=w1e(cpt,:)-w1e(cpt,centralpixel)+w1m;
dw2(cpt) = w1e(cpt,end-10)-w1e(cpt,10); %calculation of concentration
difference between top and bottom wall
dw2(cpt) = abs(dw2(cpt));
fid=fopen('DelC_step_2.txt','A');
```

```
fprintf(fid,'%6E',dw2(cpt));
```

fprintf(fid,'\r\n');

fclose(fid)

end

% step 3 after vanishing temperature gradient i.e. pure diffusion step

```
for cpt=td+3:1:tend
```

```
n1='phase_ini-phase';
```

```
n2 = num2str(cpt);
```

while length(n2)<4

```
n2 = ['0' n2];
```

end

n3='.txt';

```
nametot=[n1 n2 n3];
```

```
name1=nametot;
```

```
UPhi1=dlmread(name1);
```

UPhi1mean1=mean(UPhi1);

```
n(cpt,:)=UPhi1mean1*lambda/(2*pi*depth);
```

```
w1e(cpt,:)=n(cpt,:)/dndC;
```

```
w1e(cpt,:)=w1e(cpt,:)-w1e(cpt,centralpixel)+w1m;
```

```
%sw=size(w1e)
```

dw2(cpt) = w1e(cpt,end-10)-w1e(cpt,10);

```
dw2(cpt) = abs(dw2(cpt));
```

```
fid=fopen('DelC_step_3.txt','A');
```

```
fprintf(fid,'%6E',dw2(cpt));
```

fprintf(fid,'\r\n');

fclose(fid)

end

%figure

```
%plot(L,w1e(309,:),'b',L,w1e(319,:),'r',L,w1e(329,:),'g',L,w1e(339,:),'y',L
```

```
%,w1e(349,:),'b',L,w1e(359,:),'r',L,w1e(369,:),'b',L,w1e(400,:),'r',L,w1e(450,:),'g',L,w1e(480,:),'y
```

')

figure

```
%plot(cpt,dw3(:),'o')
```

plot(dw2,'o') %plot of concentration difference Vs number of images for entire experiment title('Concentration difference Vs time plot in isothermal condition')

xlabel('Time (minute)')

ylabel('Delta C')

A.3.2 Cost function to calculate $D_{\rm M}$

%%% Part 1: main function%%% function f=amin(D) % initial composition of the sample w1m=0.5; %nb of pixels in the x-direction x=210; %length along the gradT:1 l=0.01*0.5; % coordinates of the pixels L % 317 pixels for all the cell %1 pixel = 0.005/317 =1.577 * 1e-5 m Linter=linspace(7.8864e-6,0.005-7.8864e-6,317); L=Linter(1:304); centralpixel=316/2; %optical path

depth=0.01;

%temperature difference between the bottom and top plates

DT=10;

% n = (dn/dC)*w1

dndC= 0.0625;

%Soret coefficient

S=3.9*1e-3;

lambda=639*1e-9;

%time vector: t

t=linspace (0,14340,240);

%initialization of the cost function:

e=0;

for cpt=1:1:length(t)

name1=sprintf('Int0%3dPHA.txt',cpt+240);

UPhi1=dlmread(name1);

UPhicropped=UPhi1(:,28:end);

%for i=1:1:x

```
UPhi1moyen=mean(UPhicropped);
```

%end

n=UPhi1moyen*lambda/(2*pi*depth);

w1e=n/dndC;

```
w1e=w1e-w1e(centralpixel)+w1m;
```

%analytical solution at t=t(cpt)

```
w1cint=w1(w1m,D,S,DT,l,L,t(cpt));
```

w1c=w1cint';

%lc=size(w1c)

%lm=size(w1e)

```
e=e+(w1e-w1c)*(w1e-w1c)';
```

clear w1c

end

f=e;

end

%%% Part 2: recall of analytical calculation for each images and pixels%%%

```
function w=w1(w1m,D,S,DT,L,z,ti)
```

S1=zeros(length(z),1);

S=S*(w1m*(1-w1m));

for k=1:1:length(S1)

S1(k)=S1(k)+w1m;

end

```
for cpt=1:1:length(z)
```

for k=1:1:999

```
S1(cpt) = S1(cpt) + 2*DT*S*((((-1)^k)-1)/((k^2)*(pi^2)))*(cos(k*pi*z(cpt)/L))*exp(-1))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos(k*pi*z(cpt)/L))*(cos
```

```
(k^2)*(pi^2)*D*ti/(L^2));
```

end

end

w=S1;

A.3.3 Analytical calculation of 1-D transient concentration

function Analytical

clear all;

close all;

clear

clc

C0=0.5; % initial concontration in mass fraction

%Dt=3.98e-12;

Dm=3.27e-10; % Molecular diffusion coefficient

S1=3.37e-3; % Soret coefficient

S=C0*(1-C0)*S1;

L=0.005-(0.005*1/5); % height of the cell along vertical direction

DelT=2; % temperature difference

td=6*60*60; % time to reach steady state condition

tend=12*60*60; % total time

z1=1:1:824; % number of pixels in vertical direction

z=z1/1024*L; % length of every pixels in meter

%%% Step-1

for i =1:length(z)

for t=0:60:td

sum =0;

for n=1:2:101

```
sum=sum+1/n^2*cos(n*pi*z(i)/L)*exp(-n^2*pi^2*Dm*t/L^2);
```

end

```
C(i,t/60+1)=C0+S*DelT*(0.5-z(i)/L-4/pi^2*sum);
```

end

end

DelCst=C(i-5,end)-C(5,end);

%%% step-2

for i =1:length(z)

for t=td+60:60:tend

t2=t-td;

```
sum =0;
```

for n=1:2:101

```
sum=sum+1/n^2*cos(n*pi*z(i)/L)*exp(-n^2*pi^2*Dm*t2/L^2);
```

end

```
C(i,t/60+1)=C0-DelCst*4/(pi^{2})*sum;
```

end

end

for t=0:60:tend

t1=t/60+1;

DelC(t1)=C(i-5,t1)-C(5,t1);

DelC(t1)=abs(DelC(t1));

fid=fopen('DelC-analytical.txt','A');

```
fprintf(fid,'%10E',DelC(t1));
```

fprintf(fid,'\r\n');

```
fclose(fid)
```

end

```
t=0:60:tend;
```

```
plot(t/60,DelC,'o')
```

title('Analytical Concentration difference Vs time plot')

```
xlabel('Time (minute)')
```

ylabel('Delta C')

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