Study of physical parameters of Quaternary organic mixtures and to compare the result with the iterative equations

Project work submitted by

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Certificate

This is to certify that this project work entitled **"Study of physical parameters of Quaternary organic mixtures and to compare the result with the iterative equations"** is carried out under the guidance of **Dr. P. Richard Rajkumar** M.Sc., M.Phil., Ph.D., Associate Professor at Department of PG Physics by **Madhava Krishnan N S** (22PGP17) in partial fulfilment of the requirement for the award of the degree of Master of Science in Physics during the period 2022-2024.

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Dr. (Mrs.) S. Paul Mary Deborrah,   **Dr. P. Richard Rajkumar, (Guide)**

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Declaration

      I hereby declare that this project work for the degree of Master of Science in Physics entitled **"Study of physical parameters of Quaternary organic mixtures and to compare the result with the iterative equations"** is my original work and submitted by me to the department of PG Physics, The American College, for the award of the degree of Master of Science in Physics during the period 2022-2024. I further declare that the work reported in this project has not been submitted and will not be submitted, either in part or in full, for the award of any other degree or diploma in this or any other institute or university.

Place: The American College, Madurai – 625002   …………………………

Date: (Madhava Krishnan N S)

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Abstract

This project thoroughly delves into the intricate physical properties of Quaternary organic mixtures containing Xylene, Benzene, Toluene, and Propan-1-ol at two different temperature variations and varying proportions. The investigation involved meticulous measurements of critical parameters, including Ultrasonic velocity, Refractive index, Density, Viscosity, Rao's constant, Adiabatic compressibility, Internal pressure, and Free volume, both at 293.15 K and 303.15 K. The physical parameters were cross-examined with the values predicted by established iterative equations such as Nomoto's, Van Deal's, Arago and Biot (A&B), Lorentz-Lorentz (L-L), and Gladstone-Dale (G-D) equations. The study's outcomes not only offer profound insights into the intricate relationships and synergies within Quaternary organic mixtures but also significantly contribute to the broader understanding of their multifaceted physical properties and complex behaviours.

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CHAPTER – 1

INTRODUCTION

1.1 Introduction to Organic Mixtures and Their Significance:

In the realm of scientific exploration, the study of organic mixtures is critical for unraveling their complex interactions at the molecular level. These mixtures, comprising Benzene, Xylene, Toluene, and Propan-1-ol, hold pivotal importance in various scientific disciplines, including chemical engineering and material science. This research delves into comprehensively understanding the physical properties of these mixtures, which play a crucial role in the development of industrial processes and the formulation of advanced materials.

1.2 Importance of Analyzing Physical Parameters:

The analysis of physical parameters in Quaternary organic mixtures holds significant implications for elucidating their structural arrangements and intermolecular dynamics. This understanding is paramount for optimizing industrial operations, ensuring the stability of chemical compositions, and designing innovative materials for diverse industrial applications.

1.3 Distinct Properties of the Selected Organic Liquids:

Benzene (C_6H_6):

Benzene serves as a fundamental building block for the synthesis of polymers and a range of chemical intermediates, owing to its stable ring structure and versatility in the production of commercial goods, including pharmaceuticals and pesticides.
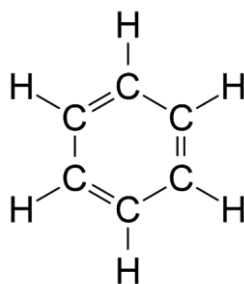

Figure 1.1: Structure of benzene

Xylene ((CH_3)$_2C_6H_4$):

Xylene, known for its high solvent power and compatibility with diverse organic solvents, is a vital ingredient in the production of paints, rubber, and leather goods. Its multi-structural forms, including ortho-xylene, meta-xylene, and para-xylene, contribute to its versatility in

numerous industrial applications. This compound serves as a fundamental building block in the synthesis of various materials, owing to its unique chemical properties and widespread applicability in the manufacturing sector.
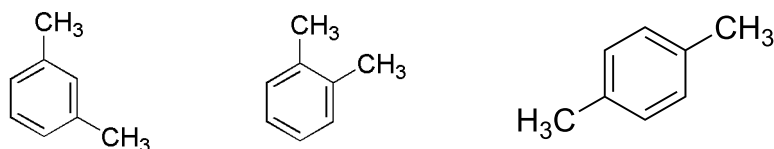

Figure 1.2: Structures of Xylene (m-xylene, o-xylene and p-xylene)
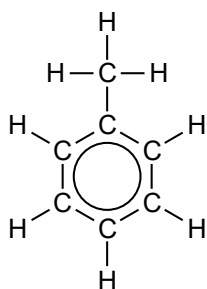
Toluene ($C_6H_5CH_3$):

Figure 1.3: Structure of toluene

Toluene's excellent solvent properties make it an essential ingredient in the production of paints, adhesives, and coatings. Its low toxicity and compatibility with diverse materials solidify its crucial role in industries where purity and solvency are paramount.

Propan-1-ol ($CH_3CH_2CH_2OH$):

Propan-1-ol's polar nature facilitates the dissolution of polar compounds, making it an essential constituent in the production of cosmetics, pharmaceuticals, and antiseptics. Its compatibility with water and various organic solvents adds to its industrial significance.
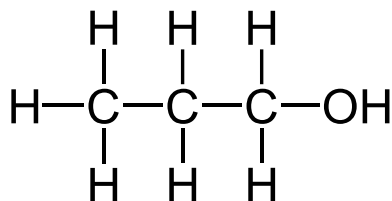

Figure 1.4: Structure of propan-1-ol

1.4 Mole fractions of the mixtures considered in this study:

The following table presents the exact mole fractions of the 9 mixtures considered in this study:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol
1	Mixture – 1	0.2610	0.1920	0.2240	0.3230
2	Mixture – 2	0.3463	0.1698	0.1982	0.2857
3	Mixture – 3	0.2381	0.2628	0.2044	0.2947
4	Mixture – 4	0.2347	0.1727	0.3022	0.2904
5	Mixture – 5	0.2247	0.1653	0.1929	0.4171
6	Mixture – 6	0.1748	0.2144	0.2501	0.3606
7	Mixture – 7	0.2827	0.1248	0.2427	0.3498
8	Mixture – 8	0.2867	0.2109	0.1476	0.3548
9	Mixture – 9	0.2997	0.2205	0.2573	0.2225

Table 1.1: Mole fractions of mixtures considered in this study

Mixture – 2 had the highest mole fraction of benzene, while Mixture – 6 had the lowest. Similarly, Mixture – 3 had the highest mole fraction of xylene, whereas Mixture – 7 had the lowest. Moreover, Mixture – 4 exhibited the highest mole fraction of toluene, while Mixture – 8 had the lowest. Lastly, Mixture – 5 contained the highest mole fraction of propanol, and Mixture – 9 had the lowest concentration of propanol.

This study endeavors to uncover the intricate relationships among the selected organic liquids and the resulting Quaternary mixtures, offering insights into the fundamental principles governing their complex behavior. Additionally, the comparison of experimental results with established iterative equations aims to provide a comprehensive understanding of the intricate interplay between individual components and the resulting physical properties of these mixtures.

CHAPTER – 2

MATERIALS AND METHODS

2.1 Preparation of a mixture:

The individual liquid, maintained at a specific temperature, was measured at a specific volume according to desired proportions and then poured into a cylindrical volumetric flask. This process was repeated for the other three liquids. The entire mixed liquid was left undisturbed for 30 minutes, with the volumetric flask securely sealed with a cork, resulting in the formation of the quaternary mixture.

2.2 Temperature maintenance arrangement:

Water circulation pipe

Constant temperature water bath

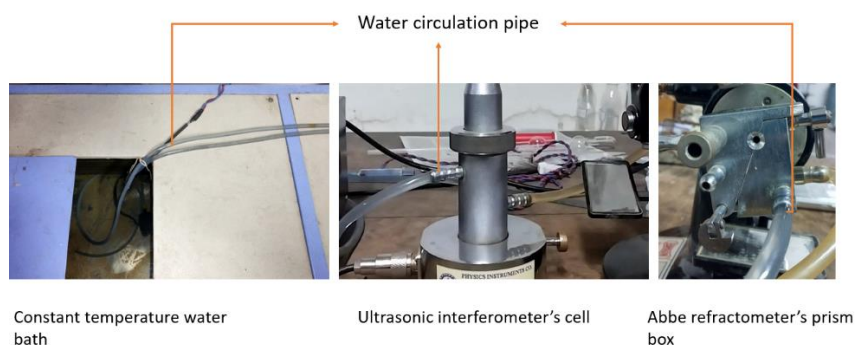Ultrasonic interferometer's cell

Abbe refractometer's prism box

Figure 2.1: Temperature maintenance arrangement

The temperature maintenance setup involved the placement of a mini submersible water pump inside the constant-temperature water bath. A pipe was connected to the submersible pump, enabling the circulation of chilled water from the temperature bath through the Abbe refractometer and ultrasonic interferometer. This arrangement ensured the maintenance of stable and controlled temperatures during the experimentation process. This is shown in Figure 2.1.

2.3 Determination of ultrasonic velocity using ultrasonic interferometer:

Micrometer scale
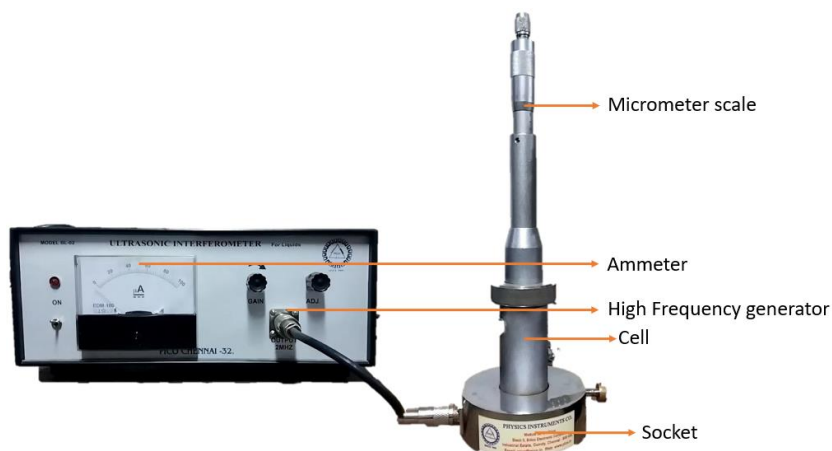
Ammeter

High Frequency generator

Cell

Socket

Figure 2.2: Ultrasonic interferometer

The cell was securely placed into the socket and fastened using the provided screw. The experimental liquid was then filled into the central part of the cell and tightly sealed with the knurled cap. Following the connection of the high-frequency generator, adjustments were made using the 'Adj' and 'Gain' knobs to ensure optimal sensitivity of the instrument. The micrometer was carefully adjusted until the maximum anode current was observed, with each adjustment considered as one oscillation. Multiple oscillations were performed, and the average distance moved on the micrometer scale was calculated. The ultrasonic velocity was then determined using the following formula

$$u = 2df$$

Where,

u is the ultrasonic velocity in m/s

f is the frequency of ultrasonic wave in Hz = 2000000 HZ (used)

d is the distance moved in micrometer scale in m

The setup is shown in Figure 2.2.

2.4 Determination of refractive index using Abbe refractometer:

The surface of the prism was cleaned first with acetone using cotton and then dried with a hairdryer. A few drops of the liquid were introduced into the prism box through the aperture. The light was allowed to fall on the mirror, which was then adjusted to reflect the maximum light into the prism box. The prism box was rotated by moving the lever knob until the boundary between shaded and bright parts appeared in the field of view. If a band of colors appeared in the light shade boundary, it was made sharp by rotating the compensator knob. The lever knob was adjusted so that the light shade boundary passed exactly through the center of the crosswire. The refractive index was read directly on the scale. The experiment was repeated for several trials, and the average value was taken. The entire setup is shown in figure 2.3.
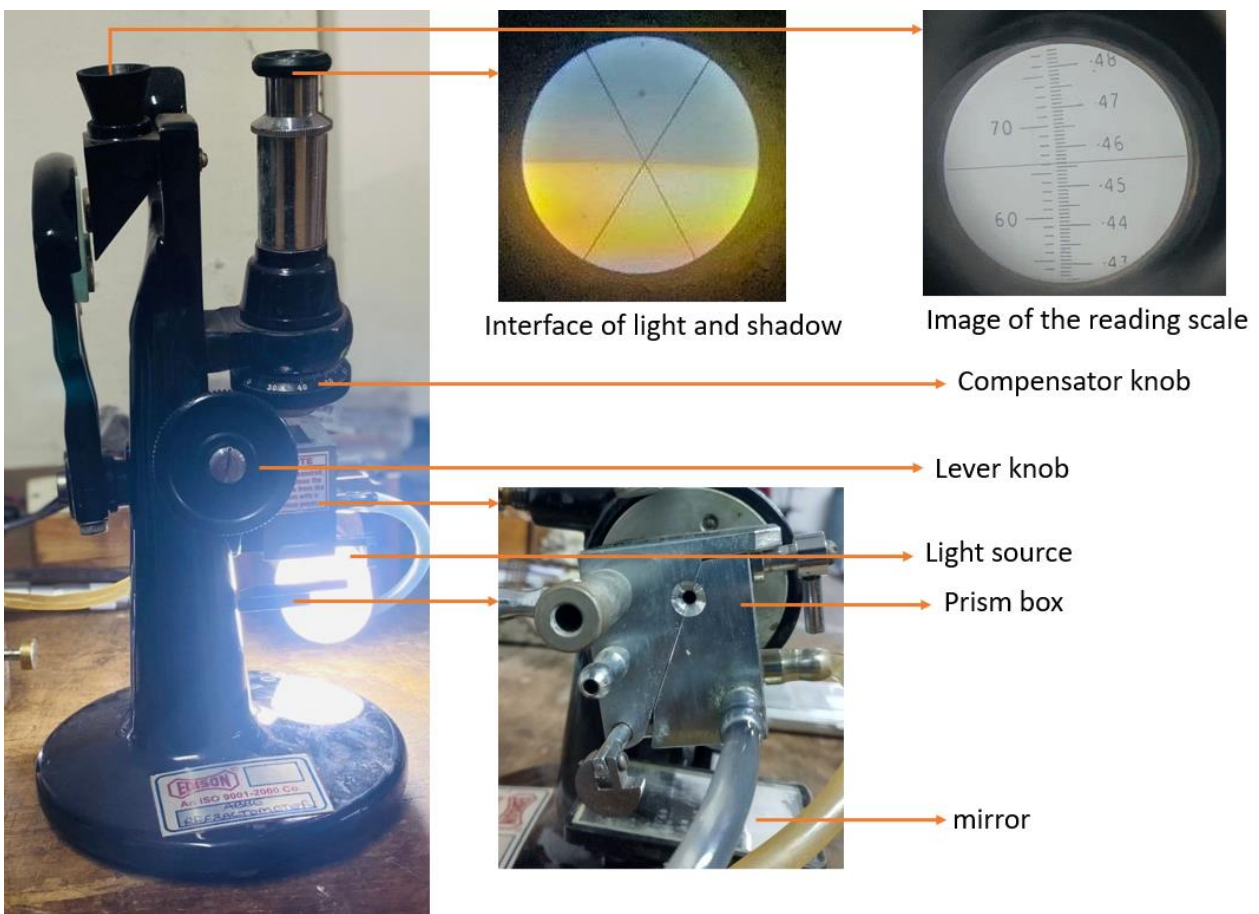
Figure 2.3: The Abbe refractometer and its components

2.5 Determination of density using pycnometer method:

Figure 2.4: Specific gravity bottle filled with liquid on electronic weighing scale

Firstly, the mass of the empty specific gravity bottle is measured using an electronic weighing scale with a least count of 0.01 mg. Subsequently, the liquid, maintained at a specific temperature, is filled into the specific gravity bottle with a predetermined volume, and the mass of the specific gravity bottle with the liquid is measured. The density of the liquid can then be calculated using the following formula.

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$$\rho = \frac{m_2 - m_1}{V}$$

Where,

ρ = density in g/ml

$m2$ = mass of specific gravity bottle with liquid in g

$m1$ = mass of specific gravity bottle without liquid in g

V = volume of liquid in ml

The specific gravity bottle is cleaned with acetone and thoroughly dried with a hairdryer. Multiple trials were conducted, and the average value was calculated. The setup is shown in figure 2.4.

2.6 Determination of viscosity using Ostwald viscometer:

The setup consists of a 'U' shaped tube with two reservoirs separated by a capillary. The liquid is drawn into the upper reservoir and allowed to flow back into the lower reservoir under the influence of gravity.

Figure 2.5: The Ostwald viscometer immersed in the constant temperature water bath

The time taken for the liquid to flow between two marks on the upper reservoir is measured to determine the viscosity. To ensure accuracy, the capillary tube was meticulously cleaned with water and acetone, and thoroughly dried with a hairdryer before each measurement.

The procedure for measuring the flow time involved immersing the viscometer in a temperature-controlled environment (at 20 and 30 degrees Celsius). Approximately 18ml of the

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solution was introduced into the viscometer, allowing it to reach the desired temperature. The flow time of the liquid was recorded multiple times, and the average value was computed. The absolute viscosity was then calculated using the following formula. For the reference liquid, water was selected. The density of water was noted as 0.9982 g/ml and 0.99567 g/ml for temperatures 293.15 K and 303.15 K, respectively [1]. The viscosity of water was observed as 1.0005 mPa s and 0.797 mPa s at 293.15 K and 303.15 K, respectively [1].

$$\eta_2 = \left(\frac{\rho_2 t_2}{\rho_1 t_1}\right)\eta_1$$

Where,

η = viscosity in m Pa   s

ρ = density

t = time of flow

1 = subscript for water (reference liquid)

2 = subscript for solution under study

The entire setup is shown in Figure 2.5.

2.7 Formulae used for calculating remaining physical parameters:

The remaining physical parameters can be calculated using following formulae.

Formula for adiabatic compressibility β:

$$\beta = \frac{1}{\rho u^2}$$

Where,

β = Adiabatic compressibility m^2/N,

u = ultrasonics velocity in m/s

ρ = density in kg/m^3

Formula for Rao's constant R:

$$R = \frac{M u^{\frac{1}{3}}}{\rho}$$

Where,

R = Rao's constant in (ml mole^{-1} (m/s)$^{(1/3)}$)

u = ultrasonics velocity in m/s

ρ = density in g/ml

M = Molecular weight in g/mole

Formula for free volume V$_f$:

$$V_f = \left(\frac{Mu}{k\eta}\right)^{\frac{3}{2}}$$

Where,

V_f = free volume in ml/mole

M = Molecular weight in gram

u = ultrasonic velocity in cm/s

η = viscosity in poise

K = 4.28*10^9 (Temperature independent constant)

Formula for internal pressure:

$$P_i = bRT \left(\frac{k\eta}{u}\right)^{\frac{1}{2}} \frac{\rho^{2/3}}{M^{7/6}}$$

P$_i$ = Internal pressure in atm

b = packing factor assumed to 2

R = Universal constant

T = Temperature in kelvin

η = viscosity in poise

u = ultrasonics velocity in m/s

M = Molecular weight in gram

K = 4.28*10^9 (Temperature independent constant)

ρ = density in g/ml

2.8 Iterative equations:

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Iterative equations are equations that relate the physical parameters of individual liquids to the mixture. In this project, the following iterative equations are considered.

Nomoto's relation:

Nomoto's relation relates ultrasonic velocity of mixture with Rao's constant of the individual liquids. This relation is given below.

$$u_{mix} = \left(\frac{\sum X_i R_i}{\sum X_i V_i} \right)^3$$

u_{mix} = Ultrasonic velocity of mixture

X_i = Mole fraction of the individual liquid

R_i = Rao's constant of the individual liquid

V_i = Molar volume of the individual liquid

This can be expanded for quaternary system as follows.

$$u_{mix} = \left(\frac{X_b R_b + X_x R_x + X_t R_t + X_p R_p}{X_b V_b + X_x V_x + X_t V_t + X_p V_p} \right)^3$$

Where,

u_{mix} = Ultrasonic velocity of mixture,

X = Mole fraction of the liquid,

R = Rao's constant of the liquid,

V = Molar volume of the liquid,

b stands for benzene,

x stands for xylene,

t stands for toluene

p stands for propan-1-ol

Van Deal's relation:

This relation relates ultrasonic velocity of mixture with individual liquids. This is given below.

$$\frac{1}{\sum X_i M_i} \frac{1}{u_{mix}^2} = \sum \frac{X_i}{M_i u_i^2}$$

Where,

M_i = Molecular weight of the individual liquid

And the remaining symbols has the same meaning as in the Nomoto's relation.

The relation can be expanded as it that has been done in the Nomoto's relation.

Arago and Biot (A&B) relation:

This relation relates refractive index and density of individual liquids with same that of mixture. The relation is given as,

$$n_{mix} = \sum \left(\frac{n_i w_i}{d_i}\right) d_{mix}$$

Where, n_{mix} = refractive index of mixture

n_i = refractive index of individual liquid

d_{mix} = density of mixture

d_i = density of individual liquid

W_i = weight fraction of individual liquid

For quaternary mixture this equation can be expanded as,

$$n_{mix} = \left(\frac{n_b w_b}{d_b}\right) d_{mix} + \left(\frac{n_x w_x}{d_x}\right) d_{mix} + \left(\frac{n_t w_t}{d_t}\right) d_{mix} + \left(\frac{n_p w_p}{d_p}\right) d_{mix}$$

Where, n stands for refractive index,

d stands for density,

w stands for weight fraction,

b stands for benzene,

x stands for xylene,

t stands for toluene,

p stands for propan-1-ol,

mix stands for mixture

Lorentz - Lorentz (L-L) equation:

      This equation also relates refractive index and density of individual liquids with same that of mixture.

$$\left(\frac{n_{mix}^2 - 1}{n_{mix}^2 + 2}\right)\frac{1}{d_{mix}} = \sum \frac{n_i^2 - 1}{n_i^2 + 2}\frac{w_i}{d_i}$$

Where the symbols have the same meaning as in the Arago and Biot (A&B) relation, and the equation can be expanded as it has been done in the Arago and Biot (A&B) relation.

Gladstone - Dale (G-D) equation:

$$\frac{n_{mix} - 1}{d_{mix}} = \sum \left\{\left(\frac{n_i - 1}{d_i}\right)w_i\right\}$$

Where the symbols have the same meaning as in the Arago and Biot (A&B) relation, and the equation can be expanded as it has been done in the Arago and Biot (A&B) relation.

CHAPTER – 3

RESULTS AND DISCUSSIONS

3.1 Physical parameters of pure liquids:

		Temperature = 293.15 K			
S. No.	Name	Ultrasonic velocity (m/s)	Refractive index	Density (g/ml)	Viscosity (m Pa s)
1	Benzene	1323.428	1.499	0.9200	0.6999
2	Xylene	1337.332	1.494	0.9200	0.7210
3	Toluene	1328.000	1.496	0.9315	0.6717
4	Propanol	1258.182	1.391	0.8760	2.3390

		Temperature = 303.15 K			
S. No.	Name	Ultrasonic velocity (m/s)	Refractive index	Density (g/ml)	Viscosity (m Pa s)
1	Benzene	1270.000	1.494	0.9000	0.5940
2	Xylene	1304.000	1.491	0.9000	0.6170
3	Toluene	1280.000	1.492	0.9230	0.5858
4	Propanol	1228.444	1.385	0.8745	1.7545

		Temperature = 293.15 K			
S. No.	Name	Rao's constant (ml mole^{-1} (m/s)$^{(1/3)}$)	Adiabatic compressibility (m2/N)	Internal pressure (atm)	Free volume (ml/mole)
1	Benzene	932.150	6.2060E-10	4243.35	0.2027
2	Xylene	1271.434	6.0776E-10	2994.83	0.3121
3	Toluene	1087.255	6.0872E-10	3450.90	0.2777
4	Propanol	740.659	7.2112E-10	10454.55	0.0208

		Temperature = 303.15 K			
S. No.	Name	Rao's constant (ml mole^{-1} (m/s)$^{(1/3)}$)	Adiabatic compressibility (m2/N)	Internal pressure (atm)	Free volume (ml/mole)
1	Benzene	939.865	6.8889E-10	4066.68	0.2437
2	Xylene	1288.799	6.5343E-10	2859.18	0.3796
3	Toluene	1083.885	6.6127E-10	3373.97	0.3226
4	Propanol	736.037	7.5776E-10	9465.24	0.0308

Table 3.1 Physical parameters of pure liquids

3.2 Ultrasonic velocities of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Ultrasonic velocity at 293.15 K (m/s)	Ultrasonic velocity at 303.15 K (m/s)
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	1287.200	1238.400
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	1290.664	1232.000
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	1299.000	1246.000
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	1296.000	1242.286
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	1283.552	1239.000
6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	1285.000	1248.880
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	1263.000	1238.000
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	1272.000	1239.000
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	1298.000	1246.000

Table 3.2 Ultrasonic velocity of mixtures at 293.15 K and 303.15 K

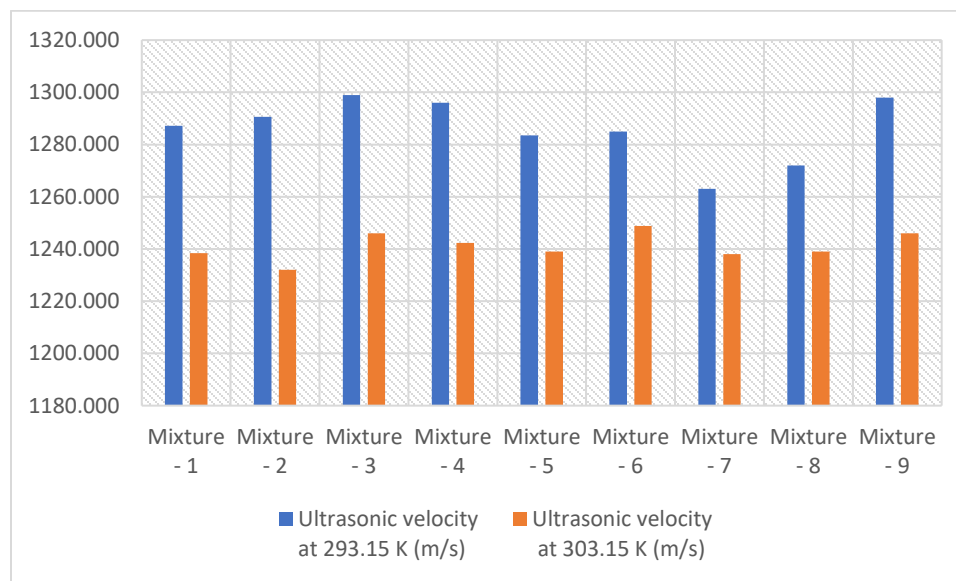The data are visualised in the Figure 3.1.

Figure 3.1 Ultrasonic velocities of mixtures

The determined ultrasonic velocities of the 9 quaternary mixtures at two different temperatures are presented in Table 3.2. An analysis of the data in Table 3.1 reveals a consistent decrease in ultrasonic velocity with increasing temperature. Similarly, this trend is observed in the

mixtures, where the ultrasonic velocity tends to increase with higher mole fractions of benzene, xylene, or toluene, and decrease with increasing mole fraction of propan-1-ol, and vice versa. Notably, the mixture with the highest ultrasonic velocity, Mixture-3, exhibited a notable predominance of xylene in its composition, while Mixture-9, characterized by the lowest mole fraction of propan-1-ol, recorded the second-highest ultrasonic velocity.

3.3 Refractive indices of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Refractive index at 293.15 K (m/s)	Refractive index at 303.15 K (m/s)
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	1.4650	1.4620
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	1.4693	1.4640
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	1.4690	1.4650
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	1.4680	1.4620
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	1.4550	1.4560
6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	1.4622	1.4590
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	1.4635	1.4590
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	1.4650	1.4580
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	1.4777	1.4710

Table 3.3 Refractive indices of mixtures 293.15 K and 303.15 K

The determined refractive indices of the 9 quaternary mixtures at two different temperatures are presented in Table 3.3. An analysis of the data in Table 3.1 reveals a consistent decrease in refractive index with increasing temperature. But this trend is not observed in all the mixtures, the refractive index values at 303.15 K appeared slightly higher compared to those at 293.15 K in Mixture -5, suggesting a minor increase with the temperature rise. It was observed that the refractive index, both at 293.15 K and 303.15 K, decreased with an increase in the mole fraction of Propanol, whereas it increased with the mole fractions of Benzene, Xylene, and Toluene in the mixtures. The data are visualised in the Figure 3.2
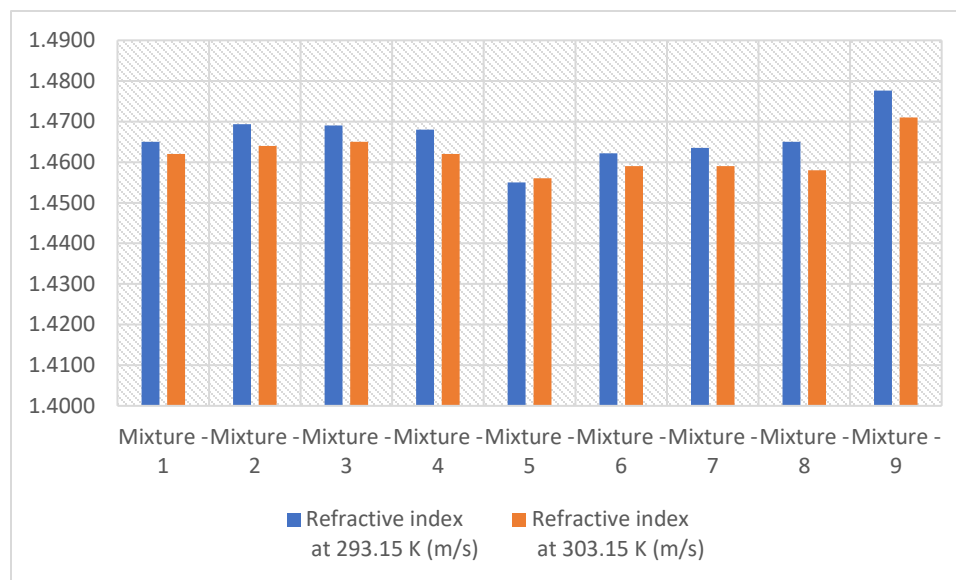
Figure 3.2 Refractive indices of the mixtures

3.4 Densities of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Density at 293.15 K (g/ml)	Density at 303.15 K (g/ml)
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	0.9205	0.9067
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	0.9727	0.9130
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	0.9725	0.9223
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	0.9359	0.9273
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	0.9235	0.9250
6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	0.9307	0.9108
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	0.9357	0.9190
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	0.9250	0.9300
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	0.9263	0.9322

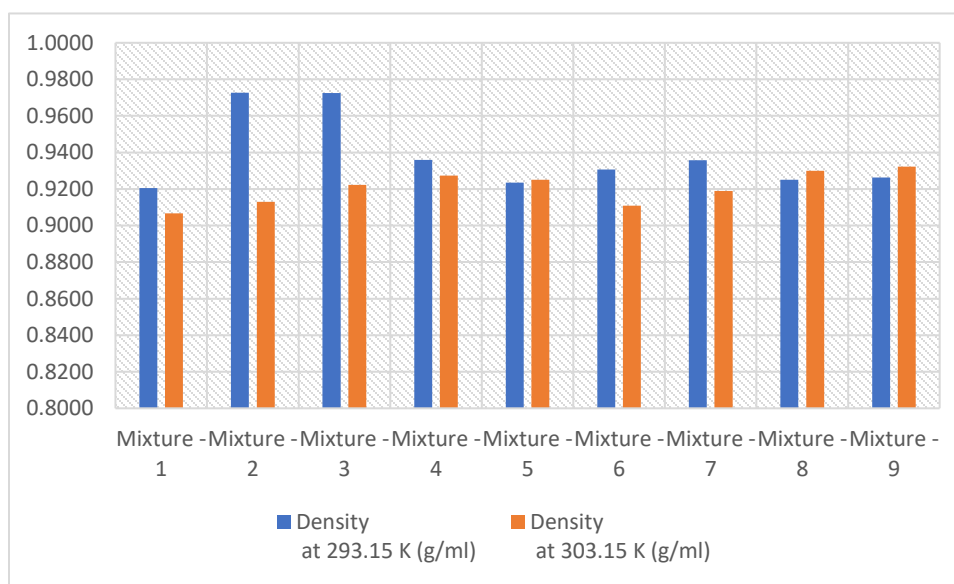**Table 3.5 Densities of mixtures 293.15 K and 303.15 K**

Figure 3.3 Densities of mixtures

The Densities of the 9 quaternary mixtures were determined and presented in Table 3.4. Analysis of the data in Table 3.1 indicated a general decrease in the Density of pure liquids with increasing temperature. However, this trend was not consistently observed in the mixtures, as the density values at 303.15 K were slightly higher than those at 293.15 K for Mixture-5, Mixture-8, and Mixture-9. It was observed that the density, both at 293.15 K and 303.15 K, decreased with an increase in the mole fraction of Propanol, while it increased with an increase in the mole fractions of Benzene, Xylene, and Toluene in the mixtures. The data are visualised in the Figure 3.3.

3.5 Viscosities of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Viscosity (m Pa s) at 293.15 K	Viscosity (m Pa s) at 303.15 K
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	0.8072	0.7121
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	0.8074	0.6740
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	0.8227	0.6810
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	0.7918	0.6345
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	0.8376	0.7158

6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	0.7649	0.6672
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	0.7449	0.6498
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	0.7520	0.6670
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	0.6969	0.6185

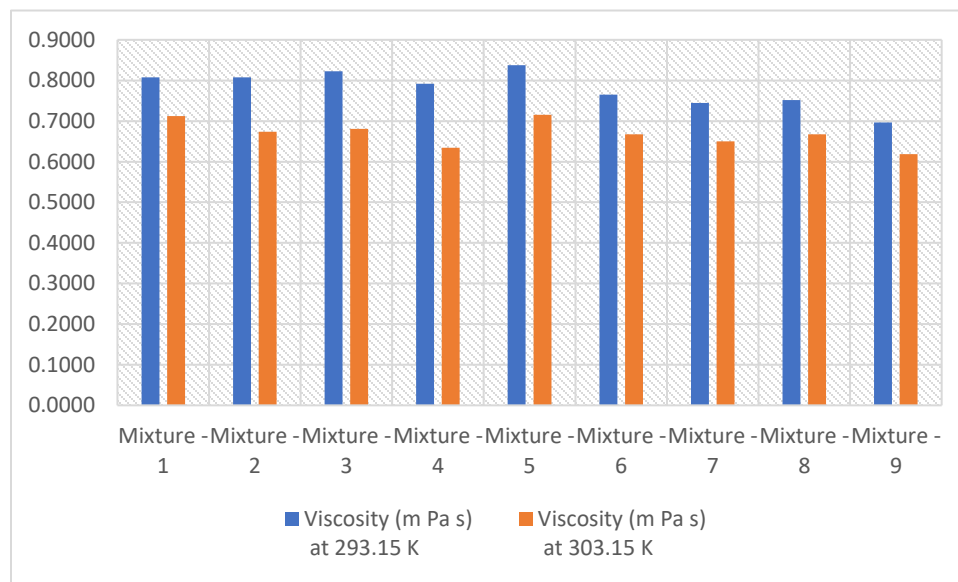**Table 3.5 Viscosities of mixtures 293.15 K and 303.15 K**

Figure 3.4 Viscosities of mixtures

The Viscosities of the 9 quaternary mixtures were determined and recorded in Table 3.5. An analysis of the data in Table 3.1 revealed a consistent decrease in the Viscosity of pure liquids with increasing temperature, a trend that was similarly observed in all mixtures. Moreover, a closer examination of the mixtures indicated that the viscosity was notably the highest in Mixture-5, characterized by the highest mole fraction of Propanol. This finding supports the understanding that an increase in the mole fraction of Propanol correlates with higher viscosities. The data are visualised in Figure 3.4.

3.6 Rao's constants of mixtures:

Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Rao's constant (ml mole^{-1} (m/s)$^{(1/3)}$) at 293.15 K	Rao's constant (ml mole^{-1} (m/s)$^{(1/3)}$) at 303.15 K
Mixture - 1	0.2610	0.1920	0.2240	0.3230	955.100	957.535

Mixture - 2	0.3463	0.1698	0.1982	0.2857	901.189	945.518
Mixture - 3	0.2381	0.2628	0.2044	0.2947	931.688	969.231
Mixture - 4	0.2347	0.1727	0.3022	0.2904	954.793	950.242
Mixture - 5	0.2247	0.1653	0.1929	0.4171	917.188	905.284
Mixture - 6	0.1748	0.2144	0.2501	0.3606	947.827	959.659
Mixture - 7	0.2827	0.1248	0.2427	0.3498	909.346	919.775
Mixture - 8	0.2867	0.2109	0.1476	0.3548	933.647	920.955
Mixture - 9	0.2997	0.2205	0.2573	0.2225	987.941	968.625

Table 3.6 Rao's constants of the mixtures 293.15 K and 303.15 K

The Rao's constants of the 9 quaternary mixtures at 293.15 K and 303.15 K were determined and recorded in Table 3.6. No notable trends were observed. Rao's constants were used for calculating the physical parameters and comparing them with iterative equations.

3.7 Adiabatic compressibilities of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Adiabatic compressibility (m^2/N) at 293.15 K	Adiabatic compressibility (m^2/N) at 303.15 K
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	6.5567E-10	7.1917E-10
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	6.1718E-10	7.2162E-10
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	6.0939E-10	6.9836E-10
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	6.3614E-10	6.9875E-10
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	6.5726E-10	7.0423E-10
6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	6.5073E-10	7.0394E-10
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	6.7000E-10	7.0998E-10
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	6.6817E-10	7.0045E-10
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	6.4074E-10	6.9096E-10

Table 3.7 Adiabatic compressibilities of mixtures 293.15 K and 303.15 K

The Adiabatic compressibilities of the 9 quaternary mixtures at 293.15 K and 303.15 K were measured and tabulated in Table 3.7. A detailed analysis of the data in Table 3.1 revealed a consistent trend of increasing adiabatic compressibility with the rise in temperature for the individual pure liquids. Similarly, this trend was consistently observed in the mixtures as well. Notably, all mixtures showed an increase in adiabatic compressibility values at 303.15 K compared to those at 293.15 K. Furthermore, it was observed that the adiabatic compressibility generally rose with the mole fraction of Propanol, while exhibiting fluctuations with the mole fractions of Benzene, Xylene, and Toluene in the mixtures. The data are visualised in Figure 3.5.
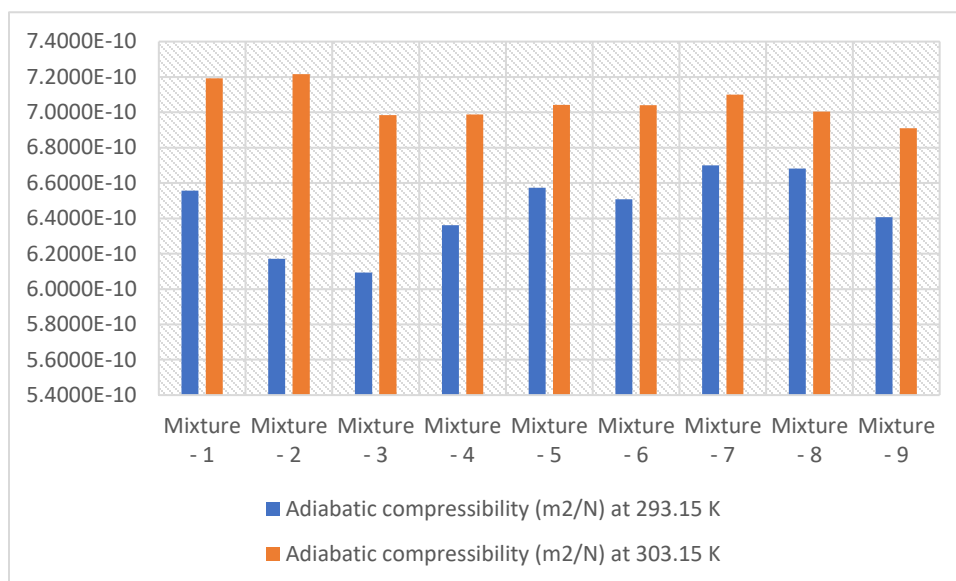
Figure 3.5 Adiabatic compressibilities of mixtures

3.8 Internal pressures of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Internal pressure (atm) at 293.15 K	Internal pressure (atm) at 303.15 K
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	4442.12	4353.12
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	4623.67	4285.45
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	4486.45	4158.41
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	4361.32	4097.84
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	4737.71	4612.80
6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	4339.68	4189.23
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	4491.29	4328.88
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	4397.82	4352.94
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	3951.55	3944.75

Table 3.8 Internal pressures of mixtures 293.15K and 303.15K

The internal pressures of the 9 quaternary mixtures at 293.15 K and 303.15 K were measured and are presented in Table 3.8. An analysis of the data revealed that the trends observed in the pure liquids, as detailed in Table 3.1, were consistent with the behaviour of the mixtures. It was noted that an increase in temperature led to a decrease in internal pressure in both pure liquids and mixtures. Furthermore, an examination of the effects of varying mole fractions of the components

indicated distinct behaviours. The presence of Propanol and Benzene generally contributed to higher internal pressures within the mixtures, while the presence of Toluene and Xylene was associated with lower internal pressures. The highest internal pressure is recorded in mixture -5, where the mole fraction of propanol is the highest. The lowest internal pressure is recorded in mixture -9, where the mole fraction of propanol is the lowest. Propanol played a dominant role in internal pressure. The data are visualised in the Figure 3.6.
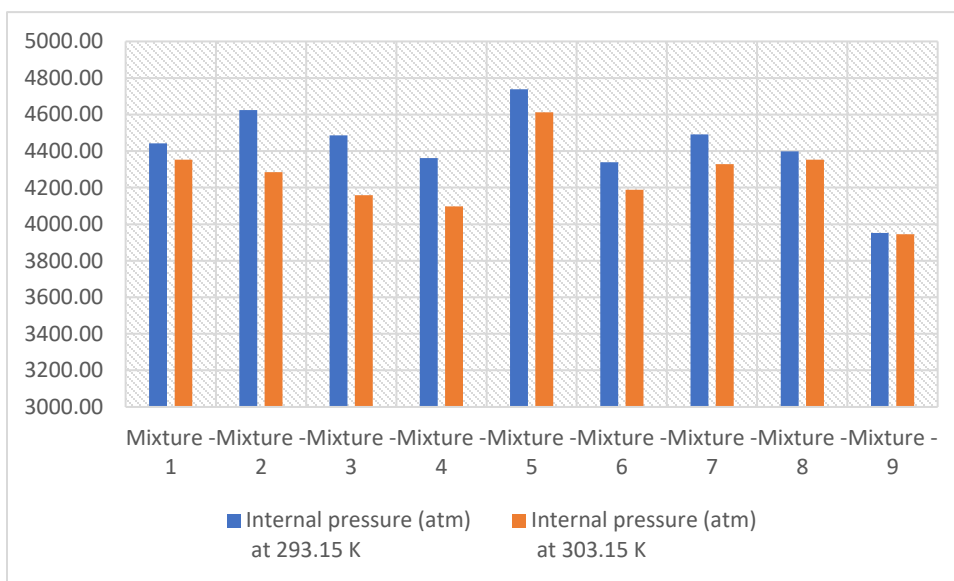

Figure 3.6 Internal pressures of mixtures

3.9 Free volumes of mixtures:

S. No.	Name	mole fraction of benzene	mole fraction of xylene	mole fraction of toluene	mole fraction of propanol	Free volume (ml/mole) at 293.15 K	Free volume (ml/mole) at 303.15 K
1	Mixture - 1	0.2610	0.1920	0.2240	0.3230	0.1652	0.1883
2	Mixture - 2	0.3463	0.1698	0.1982	0.2857	0.1649	0.2017
3	Mixture - 3	0.2381	0.2628	0.2044	0.2947	0.1696	0.2116
4	Mixture - 4	0.2347	0.1727	0.3022	0.2904	0.1755	0.2296
5	Mixture - 5	0.2247	0.1653	0.1929	0.4171	0.1474	0.1771
6	Mixture - 6	0.1748	0.2144	0.2501	0.3606	0.1797	0.2115
7	Mixture - 7	0.2827	0.1248	0.2427	0.3498	0.1741	0.2074
8	Mixture - 8	0.2867	0.2109	0.1476	0.3548	0.1768	0.2036
9	Mixture - 9	0.2997	0.2205	0.2573	0.2225	0.2206	0.2482

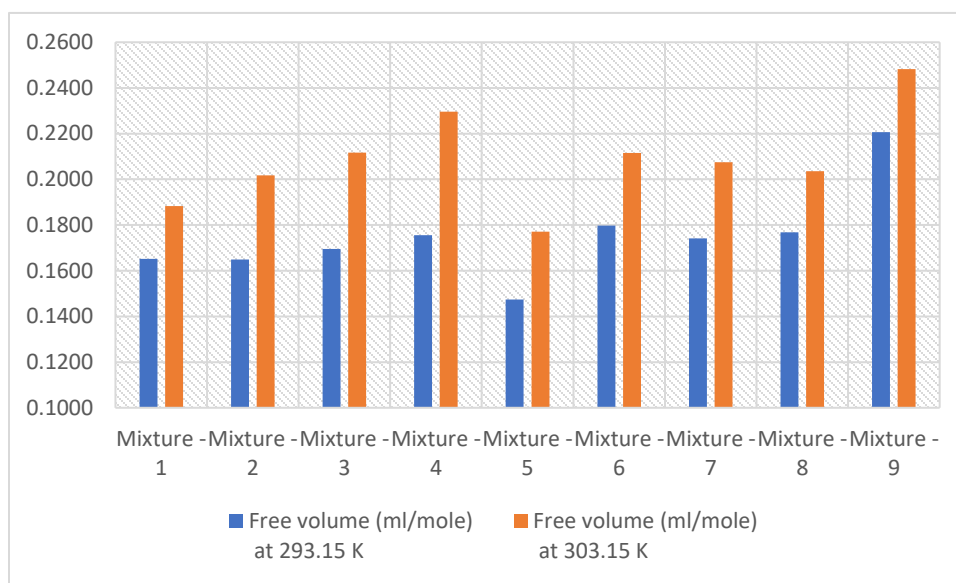**Table 3.9 Free volumes of mixtures 293.15K and 303.15K**

Figure 3.7 Free volumes of mixtures

The analysis of the individual pure liquids' free volume data revealed a consistent increase in free volume with the rise in temperature, a trend that was also observed in the mixtures. An increase in the mole fraction of Propanol was found to coincide with a noticeable reduction in the free volume, as evidenced in Mixtures 5 and 9. An increase in the mole fractions of Benzene, Xylene, and Toluene in Mixtures 6 and 9 was associated with an expansion in the free volume. Notably, the distinctive behaviour observed in Mixture 4, characterized by a significant mole fraction of Toluene. The data are visualised in Figure 3.7.

3.10 Comparison with Nomoto's relation:

S. No	Name	Experimental Ultrasonic velocity (m/s)	Theoretical Ultrasonic velocity (m/s)	Absolute Error in percentage
1	Mixture – 1 (at 293.15 K)	1287.2000	1311.6300	1.8626
2	Mixture – 2 (at 293.15 K)	1290.6640	1312.9374	1.6965
3	Mixture – 3 (at 293.15 K)	1299.0000	1314.5107	1.1800
4	Mixture – 4 (at 293.15 K)	1296.0000	1313.4375	1.3276
5	Mixture – 5 (at 293.15 K)	1283.5520	1305.6467	1.6922
6	Mixture – 6 (at 293.15 K)	1285.0000	1310.3233	1.9326
7	Mixture – 7 (at 293.15 K)	1263.0000	1308.7535	3.4960
8	Mixture – 8 (at 293.15 K)	1272.0000	1309.8241	2.8877
9	Mixture – 9 (at 293.15 K)	1298.0000	1317.6314	1.4899
10	Mixture – 1 (at 303.15 K)	1238.4000	1270.5572	2.5310
11	Mixture – 2 (at 303.15 K)	1232.0000	1270.4953	3.0299
12	Mixture – 3 (at 303.15 K)	1246.0000	1274.2846	2.2196
13	Mixture – 4 (at 303.15 K)	1242.2856	1271.5995	2.3053
14	Mixture – 5 (at 303.15 K)	1239.0000	1265.8591	2.1218
15	Mixture – 6 (at 303.15 K)	1248.8800	1270.6191	1.7109
16	Mixture – 7 (at 303.15 K)	1238.0000	1266.8371	2.2763
17	Mixture – 8 (at 303.15 K)	1239.0000	1269.5154	2.4037
18	Mixture – 9 (at 303.15 K)	1246.0000	1275.2669	2.2950

Table 3.10 Comparison of experimental and theoretical ultrasonic velocities

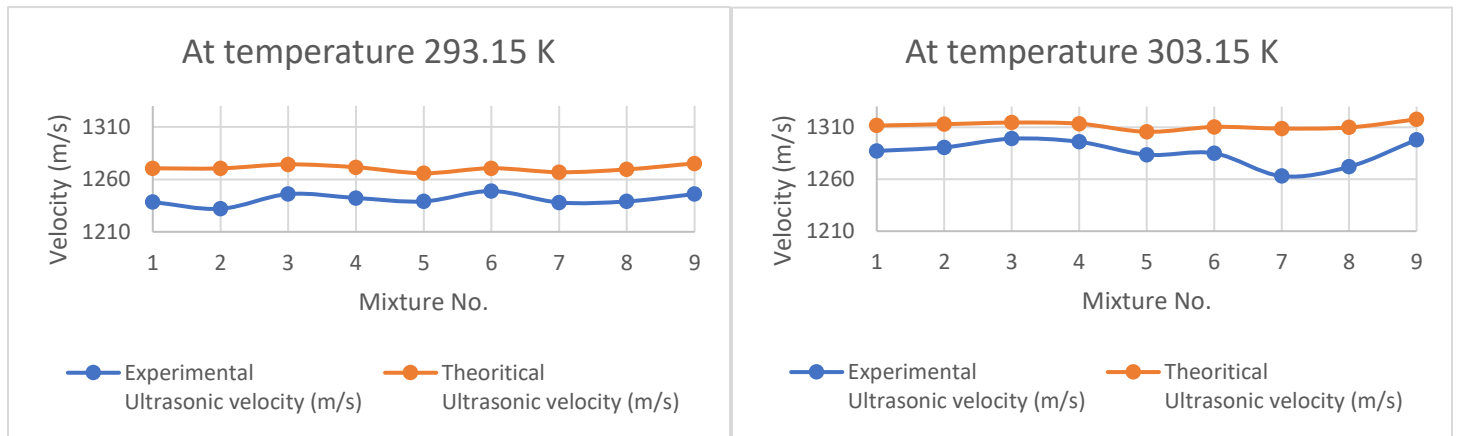**The deviations were shown in Figure 3.8.**

Figure 3.8: Deviations between Experimental and Theoretical Ultrasonic Velocities

The data in Table 3.10 represents a comparison between the experimental ultrasonic velocities and the theoretical values obtained using Nomoto's relation for the 9 mixtures at two different temperatures, 293.15 K and 303.15 K.

Upon careful examination, it is evident that there is a slight variation between the experimental and theoretical ultrasonic velocities for all the mixtures. The absolute error, represented as a percentage, shows the magnitude of this difference. Across the board, the absolute errors range from approximately 1.18% to 3.50%, indicating that the theoretical values slightly overestimate the experimental results.

Specifically, at 293.15 K, Mixtures 7 and 8 exhibit the highest absolute errors of 3.50% and 2.89% respectively, suggesting a significant deviation between the theoretical and experimental values for these mixtures. On the other hand, Mixtures 3 and 9 show the lowest absolute errors of 1.18% and 1.49% respectively, indicating a relatively close match between the theoretical and experimental ultrasonic velocities.

At 303.15 K, the absolute errors continue to fluctuate, with Mixtures 2 and 7 displaying the highest discrepancies of 3.03% and 2.28% respectively. Mixtures 6 and 9, however, demonstrate the smallest absolute errors of 1.71% and 2.29% respectively, signifying a closer alignment between the theoretical and experimental ultrasonic velocities for these mixtures at this temperature.

Overall, the comparison highlights the effectiveness of Nomoto's relation in estimating ultrasonic velocities, with the observed discrepancies likely stemming from the complexities of the actual mixture compositions and their interactions.

3.11 Comparison with Van Deal's relation:

S. No	Name	LHS	RHS	Absolute difference
1	Mixture - 1 (at 293.15 K)	7.46737E-06	7.69235E-06	2.24983E-07

2	Mixture - 2 (at 293.15 K)	7.45624E-06	7.64817E-06	1.91928E-07
3	Mixture - 3 (at 293.15 K)	7.13629E-06	7.47985E-06	3.43567E-07
4	Mixture - 4 (at 293.15 K)	7.26387E-06	7.53740E-06	2.73531E-07
5	Mixture - 5 (at 293.15 K)	7.78750E-06	8.08423E-06	2.96728E-07
6	Mixture - 6 (at 293.15 K)	7.46375E-06	7.73697E-06	2.73224E-07
7	Mixture - 7 (at 293.15 K)	7.96405E-06	7.89418E-06	6.98762E-08
8	Mixture - 8 (at 293.15 K)	7.75375E-06	7.84377E-06	9.00179E-08
9	Mixture - 9 (at 293.15 K)	7.07451E-06	7.27420E-06	1.99697E-07
10	Mixture - 1 (at 303.15 K)	8.06523E-06	8.17728E-06	1.12053E-07
11	Mixture - 2 (at 303.15 K)	8.18139E-06	8.14944E-06	3.19498E-08
12	Mixture - 3 (at 303.15 K)	7.75302E-06	7.94467E-06	1.91655E-07
13	Mixture - 4 (at 303.15 K)	7.90464E-06	8.02226E-06	1.17620E-07
14	Mixture - 5 (at 303.15 K)	8.35482E-06	8.57244E-06	2.17611E-07
15	Mixture - 6 (at 303.15 K)	7.89904E-06	8.20543E-06	3.06395E-07
16	Mixture - 7 (at 303.15 K)	8.28810E-06	8.39847E-06	1.10367E-07
17	Mixture - 8 (at 303.15 K)	8.16848E-06	8.32846E-06	1.59971E-07
18	Mixture - 9 (at 303.15 K)	7.67580E-06	7.75595E-06	8.01475E-08

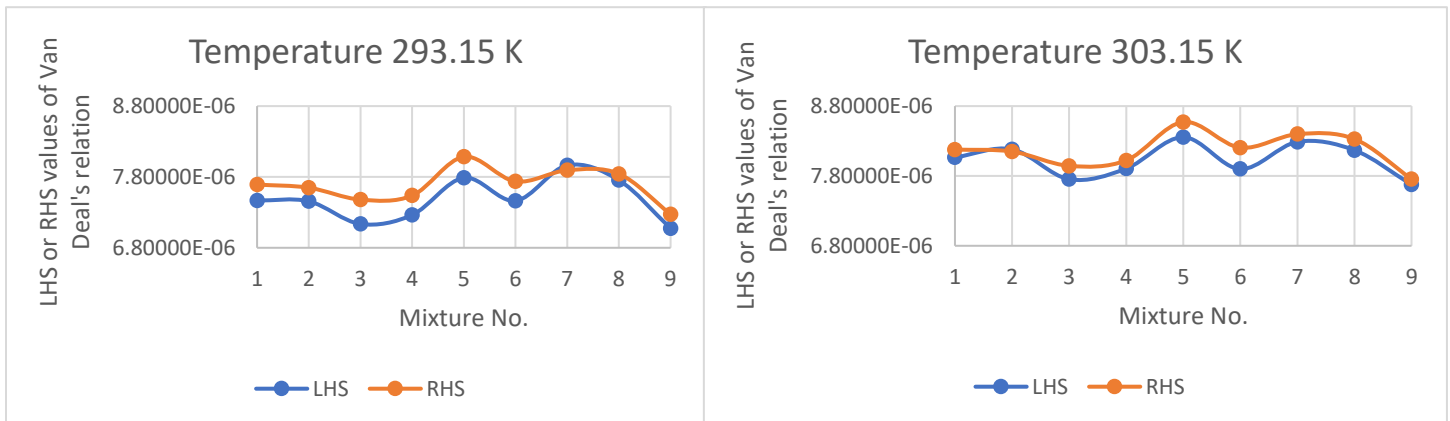**Table 3.11 Comparison of LHS and RHS values of Van Deal's relation.**

Figure 3.9 Deviations between LHS and RHS values of Van Deal's relation

The comparison between the left-hand side (LHS) and the right-hand side (RHS) values of Van Deal's relation, as presented in Table 3.11, shows that there is a difference between the calculated LHS and RHS values for each mixture at both 293.15 K and 303.15 K. The absolute differences vary across the different mixtures and temperatures. At 293.15 K, the absolute differences range from approximately 6.98762E-08 to 3.43567E-07, while at 303.15 K, they range from about 3.19498E-08 to 3.06395E-07.

Notably, Mixtures 5 and 6 demonstrate relatively higher absolute differences at both temperatures, suggesting a significant deviation between the calculated LHS and RHS values for these mixtures. On the other hand, Mixtures 7 and 9 exhibit the lowest absolute differences at 293.15 K, indicating a closer match between the LHS and RHS values for these mixtures. At 303.15 K, Mixtures 11 and 18 show the lowest absolute differences, suggesting a better agreement between the calculated LHS and RHS values for these specific mixtures. The deviations were shown in Figure 3.9.

3.12 Comparison with Arago and Biot (A&B) relation:

S. No	Name	Experimental refractive index	Theoretical refractive index	Absolute error in percentage
1	Mixture - 1 (at 293.15 K)	1.4650	1.4839	1.274
2	Mixture - 2 (at 293.15 K)	1.4693	1.5699	6.404
3	Mixture - 3 (at 293.15 K)	1.4690	1.5690	6.375
4	Mixture - 4 (at 293.15 K)	1.4680	1.5081	2.659
5	Mixture - 5 (at 293.15 K)	1.4550	1.4863	2.109
6	Mixture - 6 (at 293.15 K)	1.4622	1.4985	2.421
7	Mixture - 7 (at 293.15 K)	1.4635	1.5071	2.893
8	Mixture - 8 (at 293.15 K)	1.4650	1.4918	1.796
9	Mixture - 9 (at 293.15 K)	1.4777	1.4957	1.205
10	Mixture - 1 (at 303.15 K)	1.4620	1.4778	1.067
11	Mixture - 2 (at 303.15 K)	1.4640	1.4912	1.823
12	Mixture - 3 (at 303.15 K)	1.4650	1.5061	2.728
13	Mixture - 4 (at 303.15 K)	1.4620	1.5101	3.182
14	Mixture - 5 (at 303.15 K)	1.4560	1.5031	3.133
15	Mixture - 6 (at 303.15 K)	1.4590	1.4814	1.513
16	Mixture - 7 (at 303.15 K)	1.4590	1.4951	2.414
17	Mixture - 8 (at 303.15 K)	1.4580	1.5172	3.902
18	Mixture - 9 (at 303.15 K)	1.4710	1.5239	3.474

Table 3.12 Comparison with Arago and Biot (A&B) relation

The theoretical refractive indices calculated using the Arago and Biot (A&B) relation, as provided in Table 3.12, were instrumental in understanding the variations observed in the experimental data for the mixtures at both 293.15 K and 303.15 K. The absolute errors in percentage, ranging from 1.067% to 6.404% at 303.15 K and from 1.205% to 6.375% at 293.15 K, emphasized the deviations between the measured refractive indices and those projected by the A&B relation. deviations were shown in Figure 3.10.
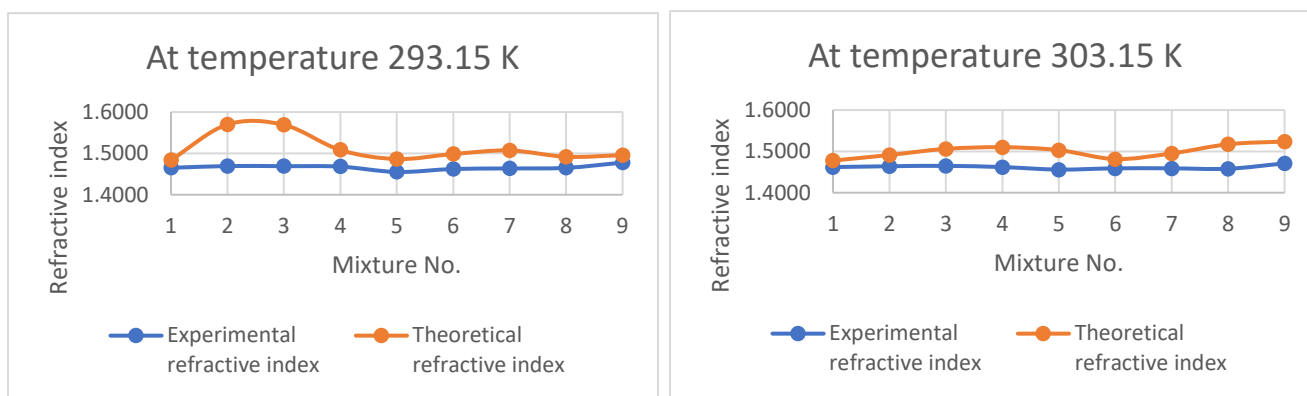
At temperature 293.15 K

At temperature 303.15 K

Figure 3.10 Deviations between experimental and theoretical refractive indices

3.13 Comparison with Lorentz – Lorentz (L-L) equation:

S. No	Name	LHS	RHS	Absolute difference
1	Mixture – 1 (at 293.15 K)	0.300326	0.305538	0.00521
2	Mixture – 2 (at 293.15 K)	0.286493	0.307063	0.02057
3	Mixture – 3 (at 293.15 K)	0.286368	0.306759	0.02039
4	Mixture – 4 (at 293.15 K)	0.297018	0.306451	0.00943
5	Mixture – 5 (at 293.15 K)	0.293794	0.301859	0.00807
6	Mixture – 6 (at 293.15 K)	0.295508	0.304011	0.00850
7	Mixture – 7 (at 293.15 K)	0.294640	0.304315	0.00968
8	Mixture – 8 (at 293.15 K)	0.298865	0.304620	0.00576
9	Mixture – 9 (at 293.15 K)	0.305391	0.309185	0.00379
10	Mixture – 1 (at 303.15 K)	0.303217	0.307445	0.00423
11	Mixture – 2 (at 303.15 K)	0.302233	0.309250	0.00702
12	Mixture – 3 (at 303.15 K)	0.299730	0.309062	0.00933
13	Mixture – 4 (at 303.15 K)	0.296458	0.308217	0.01176
14	Mixture – 5 (at 303.15 K)	0.293874	0.303225	0.00935
15	Mixture – 6 (at 303.15 K)	0.300149	0.305634	0.00549
16	Mixture – 7 (at 303.15 K)	0.297471	0.305822	0.00835
17	Mixture – 8 (at 303.15 K)	0.293400	0.306672	0.01327
18	Mixture – 9 (at 303.15 K)	0.299841	0.311626	0.01179

Table 3.13 Comparison of LHS and RHS values of L-L equation

The absolute differences ranged from 0.00379 to 0.02057 at 293.15 K and from 0.00423 to 0.01327 at 303.15 K.

Notably, Mixture - 2 exhibited the largest absolute difference at both temperatures, indicating a substantial disparity between the calculated LHS and RHS values. Conversely, Mixtures - 9 and - 1 displayed the smallest absolute differences at 293.15 K and 303.15 K, respectively, suggesting a close agreement between the LHS and RHS values for these specific mixtures.

3.14 Comparison using Gladstone - Dale (G-D) equation:

S. No	Name	LHS	RHS	Difference
1	Mixture - 1 (at 293.15 K)	0.5052	0.5154	0.0103
2	Mixture - 2 (at 293.15 K)	0.4825	0.5184	0.0359
3	Mixture - 3 (at 293.15 K)	0.4823	0.5178	0.0356
4	Mixture - 4 (at 293.15 K)	0.5000	0.5174	0.0173
5	Mixture - 5 (at 293.15 K)	0.4927	0.5080	0.0153
6	Mixture - 6 (at 293.15 K)	0.4966	0.5124	0.0158
7	Mixture - 7 (at 293.15 K)	0.4954	0.5130	0.0176
8	Mixture - 8 (at 293.15 K)	0.5027	0.5135	0.0108
9	Mixture - 9 (at 293.15 K)	0.5156	0.5228	0.0071
10	Mixture - 1 (at 303.15 K)	0.5096	0.5180	0.0085
11	Mixture - 2 (at 303.15 K)	0.5082	0.5215	0.0133
12	Mixture - 3 (at 303.15 K)	0.5042	0.5211	0.0170
13	Mixture - 4 (at 303.15 K)	0.4982	0.5197	0.0215
14	Mixture - 5 (at 303.15 K)	0.4930	0.5097	0.0167
15	Mixture - 6 (at 303.15 K)	0.5040	0.5145	0.0106
16	Mixture - 7 (at 303.15 K)	0.4995	0.5149	0.0155
17	Mixture - 8 (at 303.15 K)	0.4925	0.5163	0.0239
18	Mixture - 9 (at 303.15 K)	0.5053	0.5263	0.0210

Table 3.14 Comparison of LHS and RHS values of G-D equation

It was noted that the comparison using the Gladstone-Dale (G-D) equation for the 9 mixtures at 293.15 K and 303.15 K revealed discernible differences between the calculated left-hand side (LHS) and right-hand side (RHS) values. The differences ranged from 0.0071 to 0.0359 at 293.15 K and from 0.0085 to 0.0239 at 303.15 K.

Mixture - 2 exhibited relatively larger differences at both temperatures, suggesting some discrepancy between the calculated LHS and RHS values. On the other hand, Mixture - 9 displayed relatively smaller differences at both 293.15 K and 303.15 K, indicating a relatively closer agreement between the LHS and RHS values for this particular mixture.

CHAPTER – 4
CONCLUSIONS

Conclusions:

➢ The physical parameters of Benzene, Xylene, Toluene, and Propan-1-ol were individually measured at 293.15 K and 303.15 K. This included Ultrasonic velocity, Refractive index, Density, Viscosity, Rao's constant, Adiabatic compressibility, Internal pressure, and Free volume.

➢ The physical parameters, including Ultrasonic velocity, Refractive index, Density, Viscosity, Rao's constant, Adiabatic compressibility, Internal pressure, and Free volume, of nine distinct quaternary mixtures, comprising varying proportions of Benzene, Xylene, Toluene, and Propan-1-ol, were recorded for each mixture at 293.15 K and 303.15 K.

➢ The comparison was performed using iterative equations, including Nomoto's, Van Deal's, Arago and Biot (A&B), Lorentz-Lorentz (L-L), and Gladstone-Dale (G-D) equations, to establish relationships between the measured physical parameters and the individual liquids.

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