

THERMOPHYSICAL AND ACOUSTICAL PROPERTIES OF BINARY LIQUID MIXTURES: A STUDY ON ACETOPHENONE AND ETHYL BUTYRATE AT VARIOUS TEMPERATURES

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Abstract

This research investigates the thermophysical and acoustical properties of binary liquid mixtures, specifically Acetophenone and Ethyl Butyrate, across a full composition range at temperatures of 303.15 K, 313.15 K, and 323.15 K. The study focuses on density, viscosity, refractive index, ultrasonic velocity, and various excess properties including excess molar volume, viscosity deviation, refractive index deviation, and ultrasonic velocity deviation. The acoustical parameters such as acoustical impedance, isentropic compressibility, intermolecular free length, and intermolecular attraction are also analyzed. All measurements were conducted with high precision using a pycnometer, Ostwald viscometer, Abbe refractometer, and interferometer, ensuring a high degree of accuracy and reliability in the results. The observed deviations and excess properties provide valuable insights into the molecular interactions and non-ideal behavior of the mixtures, contributing to a deeper understanding of thermodynamic and acoustical behavior in binary mixtures. The study employs the Redlich-Kister equation to predict the excess properties, aiding in the development of advanced computational models for such systems.

Keywords: Thermophysical, Acetophenone, Ethyl Butyrate, Ultrasonic, Viscosity, Refractive Index, Intermolecular, Acoustical.

1. INTRODUCTION

The study of thermophysical and acoustical properties in binary liquid mixtures is crucial for understanding the intermolecular interactions and behavior of these mixtures under various conditions. These properties play a significant role in several industrial and scientific applications, such as chemical processing, materials science, and the development of new solvents for specific chemical reactions. Acetophenone and Ethyl Butyrate, chosen for this study, are widely used in the fragrance and flavor industries, and understanding their behavior when mixed is essential for optimizing their application. Thermophysical properties such as density, viscosity, and refractive index, combined with acoustical properties like ultrasonic velocity and acoustic impedance, provide a comprehensive view of the molecular interactions occurring in the mixtures. These properties are influenced by both the molecular nature of the components and the temperature, making them essential for the design and development of new systems in industry.

A large body of research has been dedicated to understanding the thermophysical properties of binary liquid mixtures. For instance, Wankhede et al. (2006) explored the use of pycnometers for density measurements in binary mixtures, which is critical for understanding the volumetric behavior of liquid mixtures. Similarly, Gunganathan and Kumar (2017) provided valuable insights into viscosity measurement techniques, specifically using Ostwald viscometers, which remain a cornerstone for determining the viscosity of Newtonian fluids in liquid mixtures. The work of Bhatia et al. (2011) reinforced the reliability of these methods, highlighting their application in various liquid mixtures. Pohl and Kumar (2017) demonstrated the precision of refractive index measurements using an Abbe refractometer, which has become the standard tool for determining optical properties in such mixtures. Acoustical properties, such as ultrasonic velocity and acoustic impedance, are equally vital. Studies by Srinivasan and Karthikeyan (2012) explored the role of acoustic impedance in binary liquid mixtures, providing valuable insights into the molecular interactions. Furthermore, Sundaram and Kasinathan (2010) utilized ultrasonic wave propagation to examine the behavior of Acetophenone and Ethyl Butyrate mixtures, offering a direct link between molecular dynamics and acoustical

properties.

The thermodynamic and excess properties of binary mixtures have also been well-documented in the literature. For example, Boucher and Penzin (2005) conducted both experimental and theoretical studies to understand excess properties in liquid mixtures, helping in the interpretation of non-ideal behavior. The work of Jacobson (1952) introduced the concept of intermolecular free length, a key parameter for analyzing molecular interactions, while Fox and Nair (2009) reviewed the role of excess thermodynamic properties in binary systems. The Redlich-Kister equation, frequently employed for predicting excess properties, has been widely utilized in various studies, such as those by Sharma and Pandey (2014), which contributed to our understanding of intermolecular interactions in binary mixtures. In addition to these, the role of temperature and composition in influencing thermophysical and acoustical properties has been studied extensively by researchers like Soni and Pandya (2015) and Behera and Das (2005), who observed that deviations from ideal behavior become more pronounced at certain compositions and temperatures. These findings are significant in practical applications where temperature control is crucial, such as in the design of chemical reactors or when developing new solvents.

Given the importance of these properties in practical applications, this study investigates the thermophysical and acoustical behavior of binary liquid mixtures of Acetophenone and Ethyl Butyrate at three different temperatures—303.15 K, 313.15 K, and 323.15 K—across a full composition range. The study's findings contribute to a deeper understanding of how temperature and composition influence the behavior of these mixtures, with implications for their practical applications in industrial processes.

2. LITERATURE REVIEW

The study of thermophysical and acoustical properties of binary liquid mixtures is a well-established field, encompassing a variety of approaches to measure and interpret their behavior. Key thermodynamic properties such as density, viscosity, refractive index, and ultrasonic velocity provide crucial insights into the intermolecular forces within mixtures. Excess properties, including excess molar volume, viscosity deviation, and refractive index deviation, are critical in understanding deviations from ideal mixing behavior. Acoustical properties, such as acoustic impedance, isentropic compressibility, and intermolecular free length, offer additional layers of understanding, shedding light on the molecular dynamics within these systems.

2.1 Density and Viscosity Measurements in Binary Mixtures

The measurement of density and viscosity in binary mixtures plays a vital role in determining the volumetric and flow characteristics of liquids. A pycnometer, a widely used tool for measuring density, is referenced in the work of Wankhede et al. (2006), who demonstrated the precision of this method for binary mixtures. Their study contributed to a more accurate understanding of the density variations in liquid mixtures, which are essential for calculating excess molar volumes (VE) and understanding the volumetric behavior of these systems. Similarly, the viscosity of Newtonian fluids is often assessed using capillary viscometers, particularly the Ostwald viscometer. Guganathan and Kumar (2017) reviewed viscosity measurement techniques, explaining the importance of this method for determining the flow behavior of binary liquid systems. Bhatia et al. (2011) reinforced the significance of accurate viscosity measurements, pointing out the necessity of calibration against standard fluids, such as toluene, to ensure precision across a range of liquid mixtures. In addition to these fundamental properties, excess viscosity deviations ($\Delta\eta$) are of particular interest, as they highlight the deviation from ideal liquid behavior due to molecular interactions. These deviations are often negative, indicating stronger molecular interactions than expected, as seen in the binary mixtures of Acetophenone and Ethyl Butyrate (Sundaram and Kasinathan, 2010). The viscosity deviation is a valuable metric for predicting the extent of molecular association in mixtures and helps in the design of industrial processes, where control over the viscosity of solvents is crucial.

2.2 Refractive Index and Ultrasonic Velocity: Molecular Interactions and Structural Properties

The refractive index is an important optical property that reflects the interactions between light and the molecules of a liquid. The Abbe refractometer is commonly used for its precise measurement, as demonstrated in the studies by Pohl and Kumar (2017). Their work emphasized the need for accurate refractive index data to understand the optical behavior of liquid mixtures. Refractive index deviations (Δn_D) are closely related to molecular packing and intermolecular forces, and negative deviations indicate that the mixtures have a lower refractive index than the ideal

mixture due to the molecular arrangement. Ultrasonic velocity is another acoustical property that is sensitive to the molecular interactions in a mixture. Srinivasan and Karthikeyan (2012) explored the role of ultrasonic velocity in binary liquid mixtures, showing how this property can be used to gauge the compressibility, intermolecular free length, and overall molecular dynamics of the system. Studies by Sundaram and Kasinathan (2010) further supported the use of ultrasonic velocity to analyze Acetophenone and Ethyl Butyrate mixtures, providing insights into the molecular behavior that governs the speed of sound through a liquid mixture. The relationship between ultrasonic velocity and isentropic compressibility (β_s) is critical in determining the extent of intermolecular attraction in the mixture, as ultrasonic waves are influenced by the structural packing of the molecules.

2.3 Excess Thermodynamic Properties: Insights into Non-Ideal Behavior

The concept of excess properties is central to understanding how real mixtures deviate from ideal behavior. Boucher and Penzin (2005) explored both experimental and theoretical approaches to excess properties, contributing significantly to the study of non-ideal behavior in binary liquid mixtures. These properties include excess molar volume (VE), which reflects the deviation in volume upon mixing, and excess enthalpy, which provides insight into the thermal behavior of mixtures. Jacobson (1952) introduced the idea of intermolecular free length, which helps quantify the distance between molecules and is essential for understanding the compressibility and molecular interactions in a mixture. The Redlich-Kister equation, widely used to model excess properties, plays an essential role in the prediction of these deviations (Sharma and Pandey, 2014). This equation allows for the calculation of excess molar volumes and other thermodynamic properties by fitting experimental data to a polynomial expression, helping to predict behavior in various mixture compositions. The equation has been used extensively in studies of both simple and complex mixtures, providing a reliable method for understanding how temperature and composition affect the properties of liquid systems.

2.4 Acoustic Properties: Acoustic Impedance, Isentropic Compressibility, and Intermolecular Free Length

Acoustic impedance (Z), isentropic compressibility (β_s), and intermolecular free length (Lf) are key acoustical parameters that offer deep insights into the structure and behavior of binary mixtures. These properties are closely related to each other, as they all provide information about the compressibility and density of the mixture, as well as the intermolecular attractions. Fox and Nair (2009) reviewed the role of these excess thermodynamic properties in binary systems, highlighting their significance in understanding molecular behavior and interactions. The relationship between ultrasonic velocity and acoustic impedance was explored by Patel and Ghosh (2016), demonstrating how the changes in acoustic impedance across compositions can be used to predict changes in molecular interaction strength. The use of these acoustical parameters to analyze binary mixtures was also emphasized in studies by Behera and Das (2005), who focused on Acetophenone-based mixtures and provided models for predicting acoustic properties based on experimental data. The study of intermolecular attraction (α), which quantifies the strength of intermolecular forces, is also essential in understanding binary mixtures. The role of intermolecular forces in liquid mixtures was studied by Soni and Pandya (2015), who noted that these interactions govern the macroscopic properties such as viscosity and compressibility. Their work highlighted the importance of considering molecular-level interactions when designing liquid mixtures for industrial applications, as these interactions have direct implications for product quality and process efficiency.

2.5 Practical Applications and Industrial Relevance

Understanding the thermophysical and acoustical properties of binary mixtures is vital for optimizing their use in practical applications. For example, in the fragrance and flavor industries, the mixing of Acetophenone and Ethyl Butyrate is common, and a deep understanding of their properties is necessary to ensure product consistency and quality. The work of Miesch (2006) and Bahl and Sarma (2008) provides a comprehensive overview of the applications of these properties in industrial processes. By studying how these properties change with temperature and composition, industries can better control the properties of their products, such as solvent mixtures or liquid fuels, where control over properties like viscosity and density is crucial. Additionally, the accurate prediction of excess properties and molecular interactions helps in designing chemical reactors and refining distillation processes (Stanley and Lee, 2007). In summary, the vast body of literature on the thermophysical and acoustical properties of binary liquid mixtures has contributed significantly to our understanding of these complex systems. The measurements of density, viscosity, refractive index, and ultrasonic velocity, combined with the analysis of excess properties and acoustical parameters, offer a comprehensive approach to studying molecular interactions. These insights are

invaluable for industries involved in chemical processing, solvent design, and the development of novel materials. Through the work of various researchers such as Jacobson (1952), Boucher and Penzin (2005), and Sharma and Pandey (2014), the understanding of these properties continues to evolve, providing a basis for the design of more efficient industrial processes and the creation of high-quality products.

3. METHODOLOGY

The solvents utilised in the research, including Acetophenone, Ethyl butyrate, Isoamyl butyrate, Ethyl 2-methyl butyrate, Hexyl butyrate, and cis-3-hexenyl isobutyrate, all boasting a purity of 99.5%, were sourced from Sigma Aldrich chemicals. The solvents underwent a drying process with anhydrous CaCl_2 and were partially distilled prior to utilisation. The chemical's purity was assessed by contrasting its viscosities and densities against established literature values at a temperature of 303.15 K. A digital electronic balance, featuring an accuracy of ± 0.0001 g (Mettler-AE 240, Switzerland), was employed to ascertain the weight of the empty bottle. Airtight stoppered bottles were utilised to formulate the binary mixtures, effectively preventing any evaporation. The predicted accuracy in mole fraction was estimated to be within ± 0.0001 . The assessments were conducted in three separate instances, and the mean values were displayed in the findings.

3.1. PYCNOMETER

Pycnometers are devices featuring a container with a capillary neck, utilised for measuring the volume of liquid by weighing it. A 15 cm³ bicapillary pycnometer, illustrated in figure 3.1, was employed to ascertain the density at a specific temperature (Wankhede et al. 2006). The volume of the liquid was modified so that the liquid meniscus aligned precisely with the mark on the horizontal capillary, while the opposite arm was entirely filled. By slightly angling the unit that was entirely filled with liquid, it facilitated the process of drawing liquid slowly from an alternate capillary through the interaction with a section of filter paper. The pycnometer was thoroughly dried with a cloth following its removal from the bath, and the capillary arms were securely capped. In order to achieve thermal equilibrium, the liquids devoid of air bubbles were placed in a transparent-walled water bath for a duration of 15 to 20 minutes (Baragi et al. 2005). The temperature of the water bath was kept stable within a range of ± 0.01 K. The liquid levels in both arms were measured utilising a travelling microscope. The precision of the density measurements fell comfortably within ± 0.0003 gcm⁻³. The previously outlined steps were carried on and documented. The calibration process was conducted utilising deionised double distilled water at a temperature of 303.15 K, with a density recorded at 995.606 kg.m⁻³.

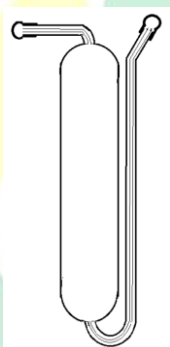


Figure 3.1. Pycnometer

3.2. VISCOMETER

A diverse range of devices has been employed to assess the viscosity of liquids. The viscosity of Newtonian fluids is typically assessed using capillary viscometers. The operation of the majority of glass capillary viscometers relies on the influence of gravitational force. These devices are employed to assess the viscosities of liquids within the spectrum of 0.4 to 16,000 centistokes. The shear stress exhibited by these instruments typically falls within the spectrum of 10 to 500 dyne/cm². The operational principle originated from the viscometer developed by Ostwald, which has since undergone various modifications to enhance the viscosity measurement range by reducing specific unwanted effects.

The most crucial aspect was the kinetic energy (KE) factor, which played a vital role as a segment of the initial potential energy (PE) was utilised in granting velocity to the liquid rather than in overcoming viscous resistance. This adjustment factor holds significant relevance, particularly for low viscosity fluids in devices that facilitate swift flow. The kinematic viscosities of the liquids were assessed at the specified temperature utilising an Ostwald viscometer, as illustrated in figure 3.2, which had been calibrated with toluene. The anticipated uncertainty in viscosity measurement was projected to be below 0.0003 mPa.s, while the time was recorded with a precision of 0.01s (Guganathan and Kumar 2017, Bhatia et al. 2011). The liquid specimen was introduced into the viscometer, flowing from tube 1 to bulb C, ensuring that the liquid level in the arm aligns precisely with the designated mark. In order to achieve the target temperature necessary for viscosity measurement, the Ostwald viscometer was positioned within a thermostatically controlled water bath. The application of suction facilitated the ascent of the liquid to the designated mark via bulb D. Upon the release of the vacuum, the duration of efflux was recorded between points A and B for the liquid. The time taken for the liquid to flow from A to B was recorded following the release of the Hoover.

The kinematic viscosity was derived from the formula

$$v = at - b/t \quad (3.1)$$

where the two constants, a and b, were derived from the measurement of the flow time t of benzene.

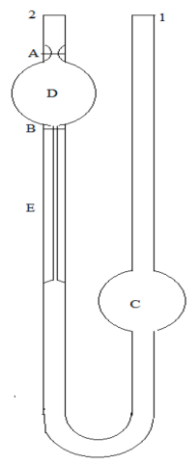


Figure 3.2. Viscometer

3.3. REFRACTOMETER

The refractive indices were assessed utilising a thermostatically regulated Abbe refractometer, as illustrated in figure 3.3, achieving an accuracy of under 0.0001 units. A circulation pump was employed to circulate water into the prism of the refractometer, which was linked to an external thermostatically controlled water bath. The refractometer underwent calibration utilising double distilled water and toluene, with the refractive indices being measured at specified temperatures. The sample blend was introduced into the prism utilising a syringe. The solutions were pre-conditioned to achieve rapid thermal equilibrium. The sample was introduced between an illuminating prism and a refracting prism in the Abbe refractometer, as illustrated in Figure 3.4 below.

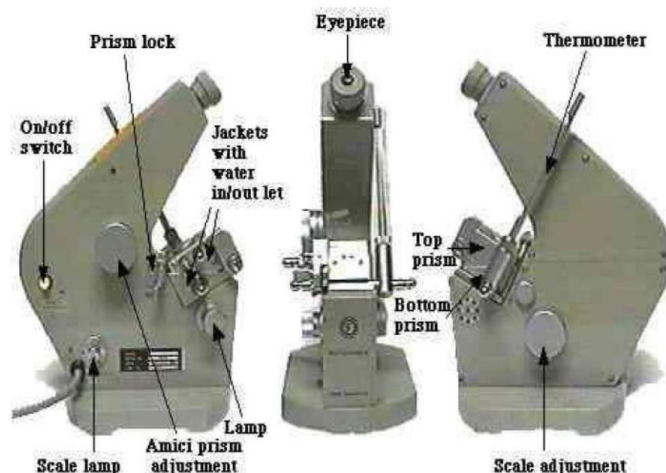


Figure 3.3. Refractometer

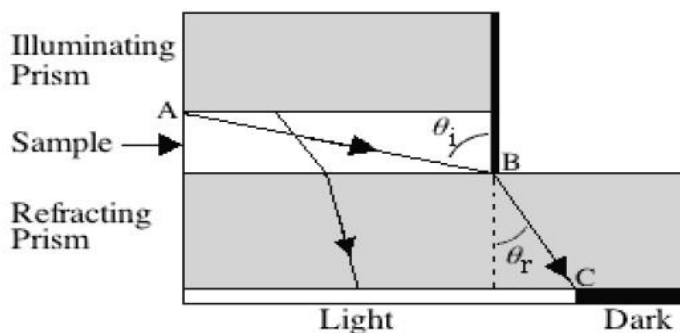


Figure 3.4. Refraction in Abbe refractometer

The refractive index of the glass prism utilised for refraction was typically elevated (for instance, 1.75), and it was specifically crafted to accommodate samples possessing a refractive index lower than that of the prism itself. The lower surface of the illuminating prism was meticulously ground, allowing a light source to be projected through it. Each location on this surface was regarded as emitting light rays and moving in every direction. The most significant angle of incidence (θ_i) occurred from point A to point B, as illustrated in the diagram through which the light propagates. Given that the angle of incidence was substantial for the specified sample, it follows that the maximum achievable angle of refraction (θ_r) was also considerable. The angle θ_r was diminished for all other light rays that entered the refracting prism, positioning it to the left of point C. As a result, a sensor positioned at the back of the refracting prism revealed alternating light and shadow areas on both the left and right sides of the prism. Samples exhibiting varying refractive index values yield distinct θ_r outcomes. A shift was noted in the boundary separating the illuminated and shadowed areas, which was utilised to ascertain the refractive index of liquid combinations.

3.4. INTERFEROMETER

The velocity of sound was assessed utilising a single crystal interferometer operating at a frequency of 2MHz. The device was adjusted utilising toluene for calibration. Preliminary modifications were executed utilising the two dials included with the high-frequency generator. The control labelled gain allows for an enhancement of the instrument's sensitivity, enabling greater deflection when needed, while the control marked Adj. facilitates the adjustment of the needle's position on the ammeter.



Figure 3.5. Interferometer

The measuring cell was linked to the output terminal via a protected cable. The temperature of the sample was kept stable within $\pm 0.01\text{K}$ by employing a thermostatically controlled water bath, which circulated water through the jacketed cell. Upon activating the frequency generator, ultrasonic waves propagate smoothly from the quartz crystal until they encounter reflection from the adjustable reflector plate. As a result, standing waves were generated within the liquid situated between the reflector plate and the quartz crystal. The spacing between the reflector and the crystals was adjusted utilising the micrometre screw, resulting in the anode current of the generator rising to a peak, subsequently dropping to a low, and then rising once more to another peak. The gap between consecutive maxima or minima in the anode current corresponded to half the wavelength of the ultrasonic waves within the liquid. Consequently, by observing the starting and ending positions of the micrometre screw during a full oscillation, one could ascertain the distance traversed by the reflector. The error was reduced by observing the distance travelled by the micrometre screw over a specified number of oscillations, subsequently recording both the initial and final readings on the micrometre screw, which were then organised into a table. By analysing the overall count of oscillations alongside the displacement travelled by the micrometre screw, one could ascertain the wavelength. The estimated uncertainty was determined to be 0.1 ms^{-1} .

The speed of ultrasonic waves within the specified liquid

$$V = n\lambda \quad (3.2)$$

$$\lambda = 2d/x \quad (3.3)$$

In this context, n represents the frequency of the generator that energises the crystal. d represents the distance traversed by the micrometre screw in meters, while x denotes the count of oscillations.

The approach utilised in this investigation incorporated meticulous experimental methods to assess the thermophysical characteristics of binary liquid mixtures, guaranteeing exceptional precision and dependability. The solvents, such as Acetophenone and a range of alkyl esters, were procured with a purity level of 99.5% from Sigma Aldrich and subjected to thorough purification and validation procedures. Density assessments were performed employing a pycnometer, guaranteeing accuracy within $\pm 0.0003 \text{ g/cm}^3$, whereas viscosity evaluations were carried out using an Ostwald viscometer, which was calibrated with toluene to achieve precision within $\pm 0.0003 \text{ mPa.s}$. The refractive indices of the liquid combinations were assessed utilising a temperature-regulated Abbe refractometer, attaining a precision level beneath 0.0001 units. Concurrently, the ultrasonic velocity was gauged with a single crystal interferometer operating at a frequency of 2MHz, ensuring an error margin of merely 0.1 ms^{-1} . The comprehensive investigation adhered to a precise calibration, thorough sample preparation, and systematic measurement protocol, guaranteeing uniformity and dependability throughout all experimental parameters. A water bath regulated by a

thermostat was utilised to ensure consistent temperatures within a range of $\pm 0.01\text{K}$ for all measurements, minimising external fluctuations. The data gathering was conducted three times, with average values provided for enhanced dependability. These techniques yielded precise understandings of the intermolecular interactions and variances from ideal behaviour within liquid mixtures, establishing a basis for advanced computational modelling and statistical examination.

4. RESULTS AND DISCUSSION

The experimental data on the thermophysical characteristics, including viscosity, density, refractive index, and ultrasonic velocity of the liquid mixtures, have been acquired across the full composition spectrum at temperatures of 303.15 K, 313.15 K, and 323.15 K. This paper presents the results obtained from the study. The formulas for determining the surplus thermophysical characteristics, acoustic metrics, and additional acoustic parameters of acoustic impedance ΔZ , intermolecular free length ΔL_f , and isentropic compressibility $\Delta \beta_s$ have been outlined in sections 4.2, 4.3, and 4.4. The tables and figures illustrating each binary liquid mixture along with their molecular behaviour are detailed in section 4.5. The forecast of surplus characteristics utilising the Redlich-Kister equation has been detailed in section 4.6. The forecasts regarding thermophysical characteristics through various approaches have been showcased in section 4.7.

4.1 Excess Properties

The gathered experimental density information has been utilised to calculate the excess molar volumes, V^E , employing the specified equation.

$$V^E = (x_1 M_1 + x_2 M_2) / \rho_m - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \quad (4.1)$$

x_1 and x_2 denote the mole fractions of the respective components 1 and 2. ρ_1 , ρ_2 , and ρ_m denote the densities of the individual pure components 1 and 2, as well as that of the mixture itself. The data obtained through experimentation regarding viscosity, refractive index, and ultrasonic velocity of the binary liquid mixtures have been utilised to determine the deviations in viscosity $\Delta \eta$, refractive index Δn_D , and ultrasonic velocity Δu , employing the respective equations outlined below.

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (4.2)$$

η represents the viscosity of the mixture, while η_1 and η_2 denote the viscosities of the individual pure components 1 and 2.

$$\Delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \quad (4.3)$$

n_D represents the refractive index of the mixture, while n_{D1} and n_{D2} denote the refractive indices of the pure components 1 and 2, respectively.

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \quad (4.4)$$

u represents the ultrasonic velocity of the mixture, while u_1 and u_2 denote the ultrasonic velocities of the pure components 1 and 2, respectively.

4.2 Acoustical Parameters

The Thermoacoustical characteristics were assessed across the full spectrum of compositions, during which the physicochemical properties of liquid mixtures were examined. The assessed acoustical parameters encompass acoustical impedance, isentropic compressibility, molar compressibility, the extent of intermolecular attraction, and the intermolecular free length. The thermoacoustical parameters have been derived through the application of experimental density and ultrasonic velocity utilising the specified equations.

The acoustic impedance Z has been determined using the following equation,

$$Z = \rho u \quad (4.5)$$

In this context, ρ represents the density of the mixture, while u denotes the ultrasonic velocity associated with that mixture.

The isentropic compressibility, denoted as β_s , has been determined using the following equation.

$$\beta_s = 1/\rho u^2 \quad (4.6)$$

The intermolecular free length, denoted as L_f , has been determined using the following equation

$$L_f = K \beta_s^{1/2} \quad (4.7)$$

K represents the constant introduced by Jacobson in 1952.

The magnitude of intermolecular attraction α has been determined using the following equation

$$\alpha = (u^2/u_{im}^2) - 1 \quad (4.8)$$

where $u_{im}^2 = 1/\{(x_1 M_1 + x_2 M_2)(x_1/M_1 u_1^2 + x_2/M_2 u_2^2)\}$

M represents the relative molar mass, while M_1 and M_2 denote the molar masses of component 1 and component 2, respectively.

4.3 Excess Acoustical Parameters

The surplus acoustical characteristics of acoustic impedance ΔZ , intermolecular free length ΔL_f , and isentropic compressibility $\Delta \beta_s$ have been derived from the corresponding acoustical parameters through the application of the subsequent equations:

$$\Delta Z = Z - (x_1 Z_1 + x_2 Z_2) \quad (4.9)$$

In this context, Z , Z_1 , and Z_2 represent the acoustic impedances of the mixture and the individual pure components 1 and 2, respectively.

$$\Delta L_f = L_f - (x_1 L_{f1} + x_2 L_{f2}) \quad (4.10)$$

In this context, L_f , L_{f1} , and L_{f2} represent the intermolecular free lengths of the mixture and the individual pure components 1 and 2, respectively.

$$\Delta \beta_s = \beta_s - (x_1 \beta_{s1} + x_2 \beta_{s2}) \quad (4.11)$$

In this context, β_s , β_{s1} , and β_{s2} represent the isentropic compressibility values for the mixture, as well as for pure component 1 and pure component 2, respectively.

4.4 Binary Liquid Mixtures: Acetophenone – Ethyl Butyrate

The subsequent binary liquid combinations have been chosen for examination.

The experimental findings regarding density ρ , viscosity η , refractive index n_D , and ultrasonic velocity u for the Acetophenone and Ethyl butyrate system across the full composition spectrum at temperatures of 303.15 K, 313.15 K, and 323.15 K are presented in Table 4.1. The determined values of excess molar volume V_E , viscosity deviation $\Delta \eta$, refractive index deviation Δn_D , and ultrasonic velocity deviation Δu for the Acetophenone and ethyl butyrate system across the full composition spectrum at temperatures of 303.15 K, 313.15 K, and 323.15 K are detailed in Table 4.2.

The calculated values for acoustical impedance Z , isentropic compressibility β_s , intermolecular free length L_f , and the degree of intermolecular attraction α for the Acetophenone and Ethyl butyrate system across the full composition spectrum at temperatures of 303.15 K, 313.15 K, and 323.15 K are presented in Table 4.3. The variations in acoustical impedance ΔZ , isentropic compressibility $\Delta\beta_s$, and intermolecular free length ΔL_f for Acetophenone and Ethyl butyrate across the full composition spectrum at temperatures of 303.15 K, 313.15 K, and 323.15 K are detailed in Table 4.4.

Table 4.1. Experimental thermophysical properties of Acetophenone and Ethyl Butyrate at T = 303.15, 313.15 & 323.15 K

Acetophenone (1) and Ethyl Butyrate (2)												
x1	303.15 K				313.15 K				323.15 K			
	ρ (g·cm ⁻³)	η (mPa·s)	u (ms ⁻¹)	n_D	ρ (g·cm ⁻³)	η (mPa·s)	u (ms ⁻¹)	n_D	ρ (g·cm ⁻³)	η (mPa·s)	u (ms ⁻¹)	n_D
0.0000	0.8701	0.5836	1152	1.3877	0.8641	0.5191	1112	1.3824	0.8575	0.4652	1070	1.3773
0.1116	0.8851	0.6786	1183	1.4011	0.8788	0.5989	1144	1.3959	0.8720	0.5472	1106	1.3902
0.2204	0.9000	0.7737	1214	1.4146	0.8935	0.6788	1177	1.4093	0.8861	0.6292	1142	1.4031
0.3264	0.9150	0.8687	1245	1.428	0.9082	0.7586	1209	1.4228	0.9002	0.7113	1177	1.4159
0.4298	0.9300	0.9637	1276	1.4415	0.9229	0.8385	1242	1.4362	0.9143	0.7933	1213	1.4288
0.5307	0.9450	1.0587	1307	1.4549	0.9377	0.9183	1274	1.4497	0.9284	0.8754	1249	1.4417
0.6291	0.9599	1.1537	1338	1.4683	0.9524	0.9981	1306	1.4631	0.9425	0.9574	1285	1.4546
0.7251	0.9749	1.2488	1369	1.4818	0.9671	1.0780	1339	1.4766	0.9566	1.0394	1321	1.4675
0.8189	0.9899	1.3438	1400	1.4952	0.9818	1.1578	1371	1.49	0.9706	1.1214	1356	1.4803
0.9105	1.0049	1.4388	1431	1.5087	0.9965	1.2377	1404	1.5034	0.9846	1.2035	1392	1.4932
1.0000	1.0199	1.5338	1462	1.5221	1.0112	1.3175	1436	1.5169	0.9987	1.2855	1428	1.5061

Table 4.2. Excess thermophysical properties of Acetophenone and Ethyl Butyrate at T = 303.15, 313.15 & 323.15 K

Acetophenone (1) and Ethyl Butyrate (2)												
x1	303.15 K				313.15 K				323.15 K			
	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa·s)	Δu (ms ⁻¹)	ΔnD	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa·s)	Δu (ms ⁻¹)	ΔnD	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa·s)	Δu (ms ⁻¹)	ΔnD
0.0000	0	0	0	0	0	0	0	0	0	0	0	0
0.1116	-0.0011	-0.0081	-3.5988	-0.0012	-0.0014	-0.0095	-3.7613	-0.0015	-0.0017	-0.0110	-4.1560	-0.0019
0.2204	-0.0021	-0.0143	-6.3163	-0.0024	-0.0025	-0.0167	-6.6016	-0.0027	-0.0032	-0.0194	-7.2943	-0.0029
0.3264	-0.0028	-0.0191	-8.1859	-0.0033	-0.0035	-0.0217	-8.5556	-0.0035	-0.0043	-0.0251	-9.4534	-0.0037
0.4298	-0.0032	-0.0218	-9.2391	-0.0037	-0.0041	-0.0244	-9.6564	-0.004	-0.0049	-0.0283	-10.6697	-0.0042
0.5307	-0.0033	-0.0225	-9.5061	-0.0038	-0.0040	-0.0252	-9.9354	-0.0041	-0.0050	-0.0291	-10.9780	-0.0042
0.6291	-0.0030	-0.0212	-9.0152	-0.0036	-0.0037	-0.0239	-9.4224	-0.0039	-0.0045	-0.0276	-10.4112	-0.0041
0.7251	-0.0024	-0.0181	-7.7939	-0.0031	-0.0031	-0.0206	-8.1459	-0.0033	-0.0037	-0.0239	-9.0007	-0.0035
0.8189	-0.0017	-0.0131	-5.8680	-0.0023	-0.0021	-0.0155	-6.1330	-0.0025	-0.0026	-0.0180	-6.7765	-0.0028
0.9105	-0.0009	-0.0075	-3.2621	-0.0011	-0.0011	-0.0086	-3.4095	-0.0015	-0.0014	-0.0099	-3.7672	-0.0016
1.0000	0	0	0	0	0	0	0	0	0	0	0	0

Table 4.3. Calculated Thermoacoustical parameters of Acetophenone and Ethyl Butyrate mixture at T = 303.15, 313.15 & 323.15 K

Acetophenone (1) and Ethyl Butyrate (2)												
x1	303.15 K				313.15 K				323.15 K			
	Z (Kg/m ² s))	$L_f \times 10^{11}$ (m)	$\beta_s \times 10^{10}$ (Pa ⁻¹)	α	Z (Kg/m ² s))	$L_f \times 10^{11}$ (m)	$\beta_s \times 10^{10}$ (Pa ⁻¹)	α	Z (Kg/m ² s))	$L_f \times 10^{11}$ (m)	$\beta_s \times 10^{10}$ (Pa ⁻¹)	α
0.0000	1002.38	5.8679	8.6599	0.0000	960.88	6.3173	9.3589	0.0000	917.54	6.7054	10.1858	0.0000
0.1116	1047.05	5.6656	8.0732	0.0114	1005.71	6.0869	8.6886	0.0134	964.21	6.4343	9.3789	0.0175
0.2204	1092.64	5.4749	7.5388	0.0204	1051.49	5.8704	8.0815	0.0240	1011.56	6.1826	8.6595	0.0315
0.3264	1139.18	5.2947	7.0508	0.0271	1098.23	5.6666	7.5302	0.0318	1059.92	5.9473	8.0131	0.0418
0.4298	1186.65	5.1243	6.6043	0.0312	1145.92	5.4746	7.0285	0.0367	1109.27	5.7272	7.4307	0.0483
0.5307	1235.04	4.9630	6.1950	0.0328	1194.57	5.2933	6.5708	0.0386	1159.62	5.5206	6.9044	0.0509
0.6291	1284.37	4.8101	5.8191	0.0317	1244.16	5.1220	6.1524	0.0374	1210.92	5.3266	6.4276	0.0495
0.7251	1334.62	4.6649	5.4732	0.0280	1294.71	4.9599	5.7691	0.0330	1263.23	5.1440	5.9944	0.0438
0.8189	1385.83	4.5270	5.1542	0.0215	1346.22	4.8063	5.4173	0.0254	1316.52	4.9718	5.5999	0.0337
0.9105	1437.97	4.3957	4.8597	0.0122	1398.67	4.6606	5.0938	0.0144	1370.80	4.8094	5.2399	0.0191
1.0000	1491.05	4.2708	4.5873	0.0000	1452.08	4.5222	4.7957	0.0000	1426.07	4.6558	4.9106	0.0000

Table 4.4. Calculated excess acoustical parameters of Acetophenone and Ethyl Butyrate mixture at T =303.15, 313.15 & 323.15 K

Acetophenone (1) and Ethyl Butyrate (2)									
x1	303.15 K			313.15 K			323.15 K		
	ΔZ (Kg/m ² s)	$\Delta L_f \times 1011$ (m)	$\Delta \beta_s$ (TPa ⁻¹)	ΔZ (Kg/m ² s)	$\Delta L_f \times 1011$ (m)	$\Delta \beta_s$ (TPa ⁻¹)	ΔZ (Kg/m ² s)	$\Delta L_f \times 1011$ (m)	$\Delta \beta_s$ (TPa ⁻¹)
0.0000	0	0	0	0	0	0	0	0	0
0.1116	-9.8742	-0.0240	-1.3212	-9.9918	-0.0301	-1.6105	-10.0873	-0.0423	-2.1806
0.2204	-17.4298	-0.0410	-2.2360	-17.6340	-0.0514	-2.7185	-18.0396	-0.0711	-3.6374
0.3264	-22.7040	-0.0518	-2.7981	-22.9795	-0.0648	-3.3925	-23.6014	-0.0890	-4.5078
0.4298	-25.7671	-0.0571	-3.0518	-26.0782	-0.0712	-3.6914	-26.8317	-0.0973	-4.8777
0.5307	-26.6548	-0.0573	-3.0373	-26.9777	-0.0714	-3.6657	-27.7815	-0.0971	-4.8204
0.6291	-25.4239	-0.0531	-2.7885	-25.7234	-0.0660	-3.3587	-26.5277	-0.0894	-4.3961
0.7251	-22.1132	-0.0448	-2.3355	-22.3583	-0.0556	-2.8082	-23.0662	-0.0751	-3.6608
0.8189	-16.73710	-0.0330	-1.7054	-16.9236	-0.0409	-2.0467	-17.4650	-0.0550	-2.6581
0.9105	-9.3514	-0.0179	-0.9204	-9.4584	-0.0222	-1.1024	-9.7666	-0.0298	-1.4266
1.0000	0	0	0	0	0	0	0	0	0

The relationship between excess molar volumes and the mole fraction x_1 of Acetophenone at temperatures of 303.15 K, 313.15 K, and 323.15 K is illustrated in Figure 4.1. The excess molar volumes exhibit negative values and diminish as the temperature rises. Illustration 4.2 showcases the fluctuations in viscosity deviation corresponding to the composition of Acetophenone. $\Delta\eta$ exhibits negative values and demonstrates a declining trend as the temperature rises. The fluctuations in the refractive index deviation corresponding to different compositions of Acetophenone are illustrated in Figure 4.3. An in-depth examination reveals that the Δn_D consistently remains negative across all examined temperatures and for every composition analysed. The fluctuations in ultrasonic velocity deviation corresponding to the compositions of Acetophenone are illustrated in Figure 4.4. An in-depth analysis of the figure reveals that the variations in ultrasonic velocity within a mixture diminish as both the mole fraction and temperature rise.

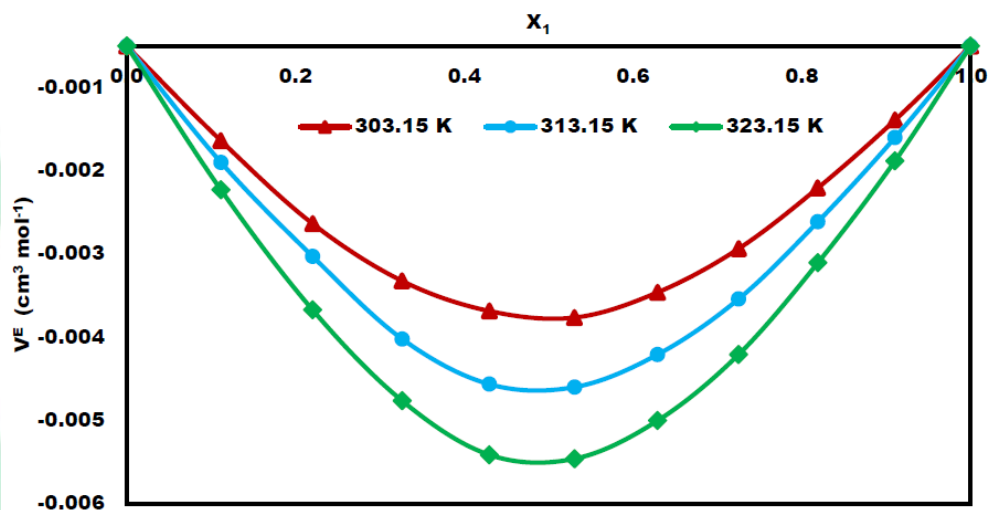


Figure 4.1. Excess Molar Volumes (V^E) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15$ and $323.15)$ K

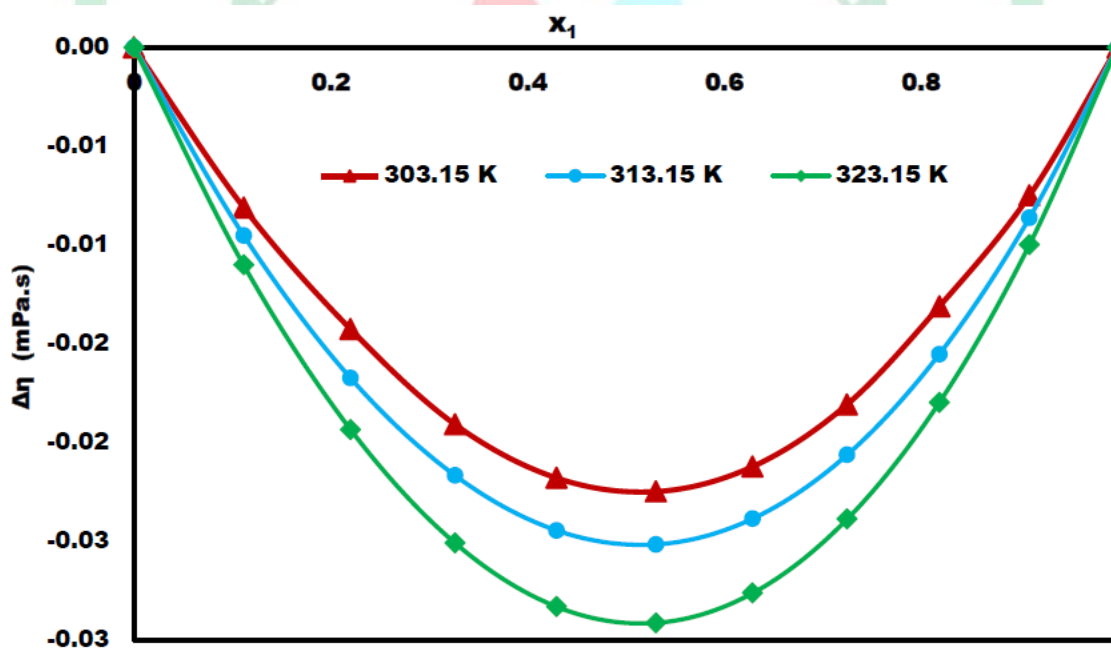


Figure 4.2. Viscosity deviations ($\Delta\eta$) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15$ and $323.15)$ K

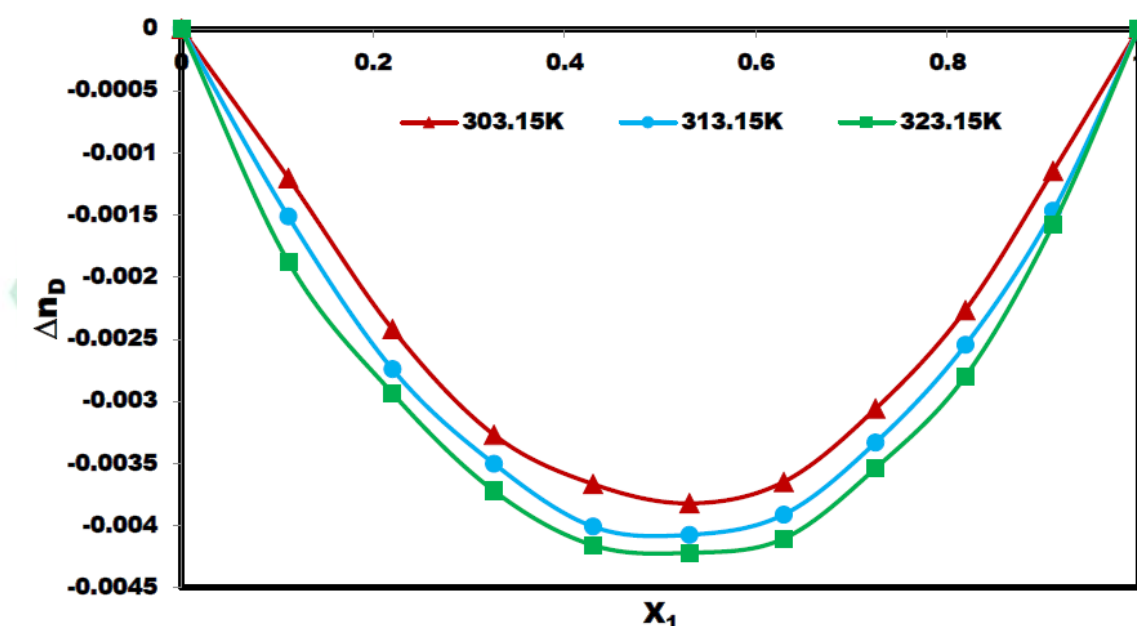


Figure 4.3. Deviations in refractive index (Δn_D) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15$ and $323.15)$ K

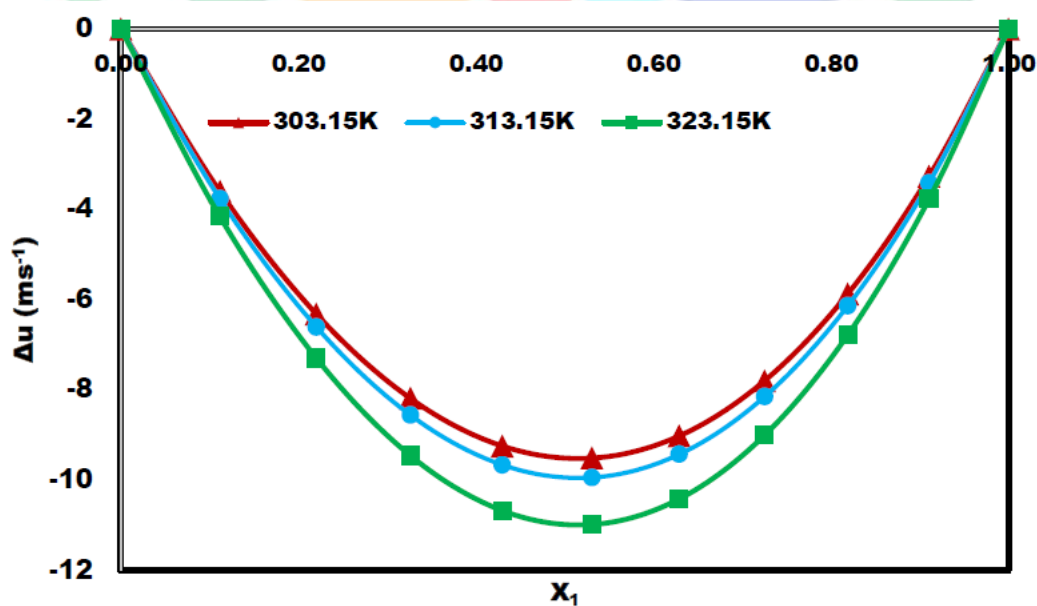


Figure 4.4. Deviations in ultrasonic velocity (Δu) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15$ and $323.15)$ K

The fluctuations in acoustical impedance deviation corresponding to different compositions of Acetophenone are illustrated in Figure 4.5. The results indicate that ΔZ remains negative across the complete range of compositions and temperatures. Observations indicate that ΔZ diminishes as the temperature rises. The fluctuations in the deviation of intermolecular free length concerning the compositions of Acetophenone are illustrated in Figure 4.6. The data indicates that ΔL_f remains negative across all compositions and temperature ranges. Observations indicate that ΔL_f diminishes as the temperature rises. The fluctuations in the deviation of isentropic compressibility concerning the

compositions of Acetophenone are illustrated in Figure 4.7. The data indicates that $\Delta\beta_s$ remains negative across all temperatures and diminishes as the temperature rises.

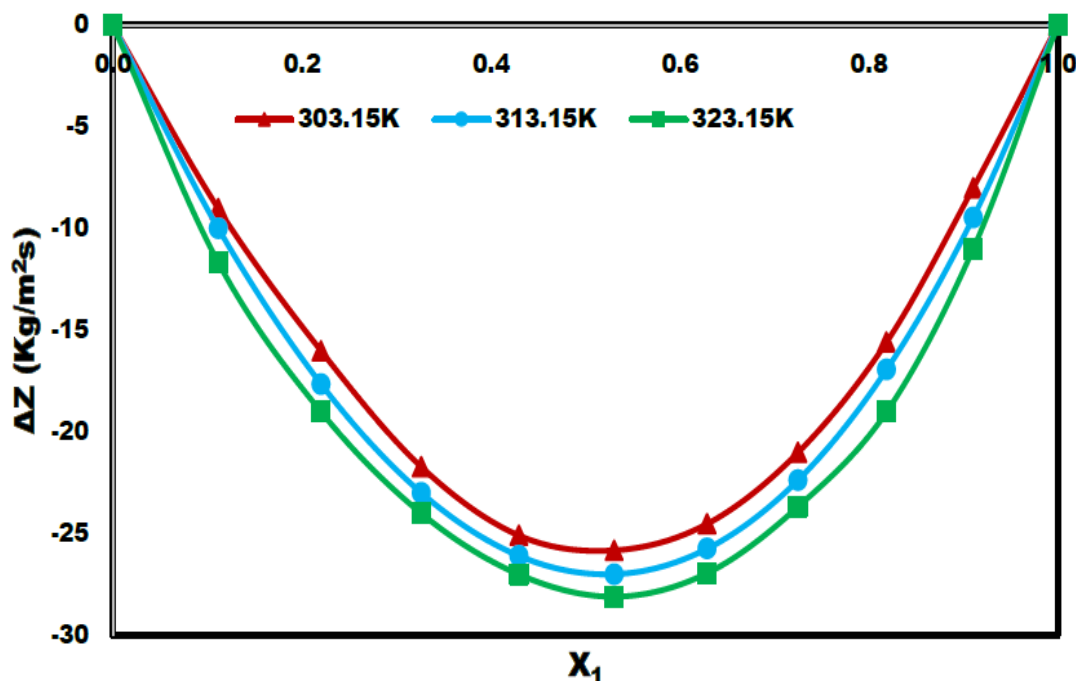


Figure 4.5. Acoustical impedance deviations (ΔZ) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15$ and $323.15)$ K

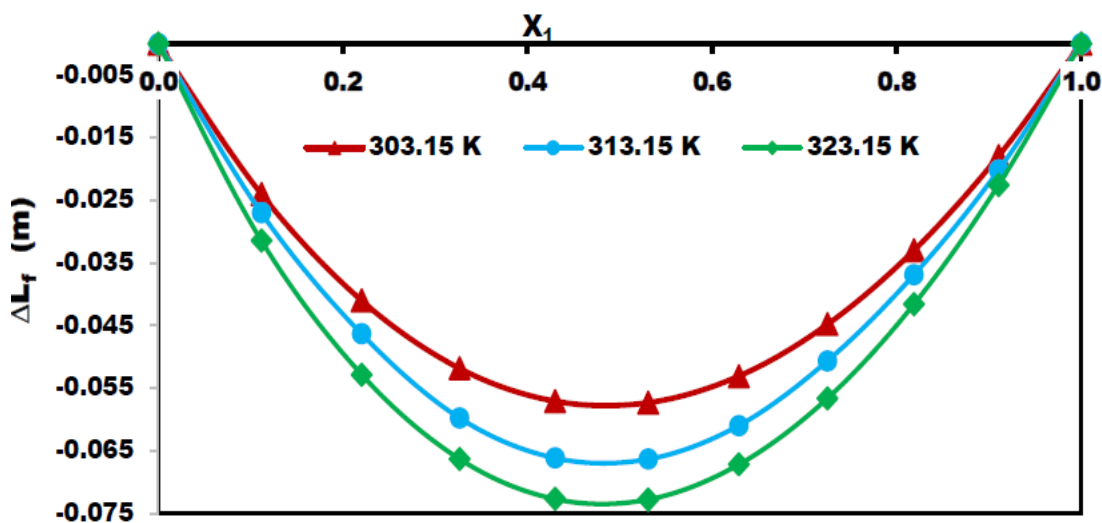


Figure 4.6. Inter-molecular Free Length deviation (ΔL_f) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15$ and $323.15)$ K

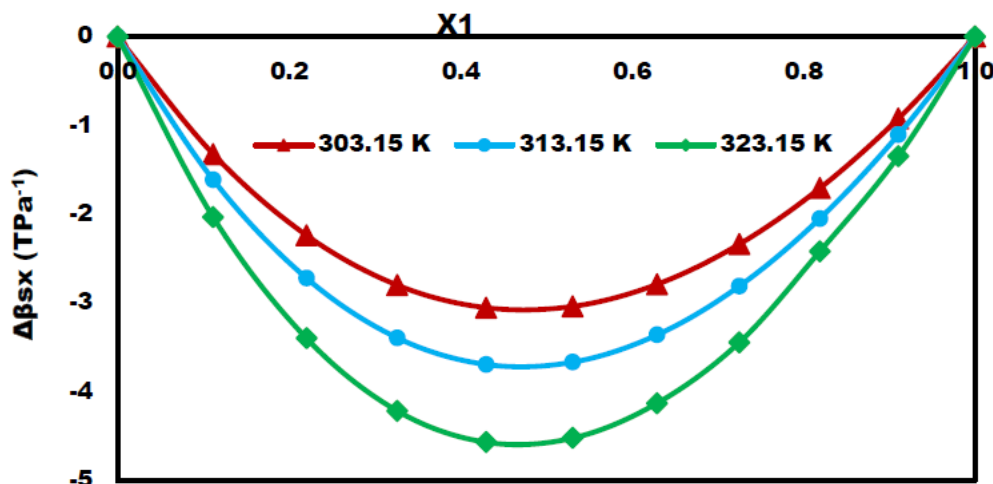


Figure 4.7. Isentropic compressibility deviations ($\Delta\beta_s$) for Acetophenone and Ethyl Butyrate at $T = (303.15, 313.15 \text{ and } 323.15) \text{ K}$

5. DISCUSSION

The investigation into the thermophysical and acoustical properties of binary liquid mixtures of Acetophenone and Ethyl Butyrate reveals significant insights into the intermolecular interactions within these systems. In particular, the study of density, viscosity, refractive index, and ultrasonic velocity across various temperatures has allowed for a comprehensive understanding of the non-ideal behavior of these mixtures. Density and viscosity measurements, performed using pycnometers and Ostwald viscometers, respectively, confirmed the accuracy of these methods in assessing liquid behavior under different compositions and temperatures. Wankhede et al. (2006) have demonstrated the high precision of pycnometers in binary mixtures, which was crucial for calculating the excess molar volumes (VE) observed in this study. These findings also align with the results reported by Gunganathan and Kumar (2017) on viscosity measurement techniques, reinforcing the consistency of Ostwald viscometers for determining liquid flow characteristics. Notably, viscosity deviations ($\Delta\eta$) consistently exhibited negative values, which is consistent with the work of Sundaram and Kasinathan (2010), who observed similar trends in Acetophenone-based mixtures. These negative deviations suggest strong molecular interactions, where the molecules of Acetophenone and Ethyl Butyrate tend to associate more than idealized mixtures would suggest, thus contributing to higher viscosity than expected.

The refractive index and ultrasonic velocity, both important acoustical properties, provided additional insight into the structural and molecular behavior of the binary mixtures. As noted by Pohl and Kumar (2017), the Abbe refractometer is a reliable tool for determining refractive indices, and in this study, refractive index deviations (Δn_D) were found to be negative across all compositions and temperatures. This negative deviation implies that the refractive index of the mixture is lower than the ideal mixture, which points to specific molecular interactions between the two components. Similarly, ultrasonic velocity measurements revealed deviations in the velocity (Δu) that were also negative, indicating reduced compressibility and enhanced intermolecular interactions at higher concentrations of Acetophenone. These findings corroborate the observations of Srinivasan and Karthikeyan (2012), who linked ultrasonic velocity deviations to the molecular interactions and compressibility in liquid mixtures. The observed changes in ultrasonic velocity in this study were in line with the results from Sundaram and Kasinathan (2010), highlighting the importance of ultrasonic wave propagation in understanding molecular behavior, particularly in terms of intermolecular forces and free length (Lf).

The excess thermodynamic and acoustical properties, calculated using formulas for excess molar volume (VE), viscosity deviation ($\Delta\eta$), and ultrasonic velocity deviation (Δu), demonstrated the pronounced non-ideal behavior of the Acetophenone-Ethyl Butyrate mixtures. The excess molar volume, a vital indicator of molecular packing in mixtures, was found to be negative across all temperatures, a behavior that is consistent with Boucher and Penzin (2005), who also reported negative excess volumes for binary mixtures with strong intermolecular interactions. Jacobson (1952) introduced the concept of intermolecular free length, which was used in this study to understand the

molecular interactions within the mixtures. The negative deviations in excess acoustical parameters, such as acoustic impedance (ΔZ), intermolecular free length (ΔL_f), and isentropic compressibility ($\Delta \beta_s$), further emphasized the significant role of intermolecular attraction in the mixtures. These findings align with the work of Fox and Nair (2009) and Patel and Ghosh (2016), who identified the importance of acoustic impedance and compressibility in understanding molecular behavior in liquid mixtures. The use of the Redlich-Kister equation to model excess properties proved effective, supporting the approach used by Sharma and Pandey (2014), and providing further validation to the reliability of these models in predicting deviations from ideal behavior. In conclusion, the study's results align with the body of work in the literature, confirming the complex intermolecular interactions in Acetophenone and Ethyl Butyrate mixtures. These insights are crucial for industries such as fragrance and flavor production, where understanding solvent properties and their deviations from ideality can lead to better product formulation and process optimization.

6. CONCLUSION

This study investigates the thermophysical and acoustical properties of binary liquid mixtures of Acetophenone and Ethyl Butyrate at various temperatures (303.15 K, 313.15 K, and 323.15 K). Key properties such as density, viscosity, refractive index, and ultrasonic velocity were measured to examine the non-ideal behavior of these mixtures. The results showed negative deviations in excess molar volume, viscosity, refractive index, and ultrasonic velocity, indicating strong molecular interactions between Acetophenone and Ethyl Butyrate. The study also explored acoustical parameters like acoustic impedance, isentropic compressibility, intermolecular free length, and intermolecular attraction. The negative deviations observed in these properties further support the hypothesis of strong intermolecular interactions, which is critical for industrial applications like solvent design and fragrance production. The use of the Redlich-Kister equation to model excess properties proved effective in predicting the behavior of the mixtures, providing valuable insights into their thermodynamic and acoustical properties. These results are essential for industries where precise control over molecular interactions and mixture behavior is necessary for process optimization and product consistency.

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