Estimation of Various Thermodynamic Properties Using Ultrasonic Velocity, Density, and Refractive Index Data

By

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Abstract

The determination of thermodynamic properties of liquid mixtures plays a crucial role in understanding molecular interactions and industrial applications such as chemical processing, pharmaceuticals, and material science. This study focuses on the estimation of key thermodynamic parameters using experimentally measurable properties such as ultrasonic velocity, density, and refractive index. Parameters including adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, excess properties, and internal pressure are evaluated. The correlation between these properties provides insight into molecular association, structural arrangement, and interaction strength within mixtures. The study demonstrates that combined analysis of acoustic, volumetric, and optical data offers a reliable and cost-effective approach for thermodynamic characterization.

Keywords

Ultrasonic Velocity, Density, Refractive Index, Thermodynamic Properties, Liquid Mixtures, Molecular Interactions, Excess Functions

Introduction

Thermodynamic properties are essential for understanding the physical and chemical behavior of substances. Traditional methods for determining these properties often require complex instrumentation and time-consuming procedures. However, indirect methods based on measurable physical properties such as ultrasonic velocity, density, and refractive index have gained prominence (Rao, 2009).
Ultrasonic studies provide valuable information about intermolecular interactions and structural changes in liquids. Density measurements help determine volumetric properties, while refractive index gives insight into molecular polarizability and composition. When combined, these parameters allow the estimation of several thermodynamic properties with high precision (Kinsler *et al*., 2010).

Objective of the study

This research aims to explore the estimation of thermodynamic properties using these measurable parameters and analyze their significance in understanding molecular interactions in liquid systems.

Theoretical Background

Ultrasonic Velocity (U)

Ultrasonic velocity in a medium depends on its elasticity and density. It is given by:

$$U = \frac{1}{\sqrt{\beta\rho}}$$

Where:

- U= ultrasonic velocity
- β= adiabatic compressibility
- ρ= density

This relationship forms the basis for determining compressibility and related thermodynamic parameters (Thirumaran and Kob, 2009).

Density (ρ)

Density is defined as mass per unit volume and is essential for calculating molar and excess properties. It plays a key role in evaluating volumetric behavior and deviations from ideality (Benson *and* Kiyohara,).

Refractive Index (n)

Refractive index relates to the optical properties of a medium and provides information about molecular structure, interactions, and polarizability (Rao and Verrall,).

Derived Thermodynamic Parameters

Using the measured data, the following thermodynamic properties can be calculated:

Adiabatic Compressibility (β)

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

It indicates the compressibility of the medium and reflects intermolecular interactions.

Intermolecular Free Length (L_f)

$$L_f = K\sqrt{\beta}$$

Where $K$is Jacobson's constant.

This parameter indicates the average distance between molecules and is useful in studying liquid structure (Kielczynski).

Acoustic Impedance (Z)

$$Z = U\rho$$

It represents resistance to sound propagation and provides insight into molecular cohesion (Kannappan, 2002).

Molar Volume (V_m)

$$V_m = \frac{M}{\rho}$$

Where $M$is molar mass.

Molar volume helps in understanding packing efficiency and molecular size (Gladstone and Dale, 2013).

Internal Pressure (π_i)

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}$$

Internal pressure reflects cohesive forces and molecular interactions in liquids (Heller).

Excess Properties

Excess properties help understand deviation from ideal behavior:

$$A^E = A_{mix} - (x_1A_1 + x_2A_2)$$

These properties are crucial for analyzing molecular interactions and non-ideal behavior in mixtures (Dubey and Sharma).

Property	Formula	Significance
Adiabatic Compressibility (β)	(1/U^2\rho)	Molecular interaction strength
Free Length (Lf)	(K\sqrt{\beta})	Distance between molecules
Acoustic Impedance (Z)	(U\rho)	Resistance to sound
Molar Volume (Vm)	(M/\rho)	Packing efficiency
Internal Pressure (πi)	Complex relation	Cohesive forces

Methodology

Materials

- Analytical grade liquids
- Binary mixture preparation using mole fraction

Instruments

- Ultrasonic Interferometer (2 MHz)
- Digital Densitometer
- Abbe Refractometer

Procedure

1. Prepare mixtures of known composition
2. Measured ultrasonic velocity
3. Measured density
4. Measured refractive index
5. Maintaining constant temperature (298.15 K)

Measurements

- **Ultrasonic velocity** measured using an ultrasonic interferometer
- **Density** measured using a pycnometer or digital densitometer
- **Refractive index** measured using an Abbe refractometer

All measurements are carried out at constant temperature (±0.1 K) to ensure accuracy and reproducibility (Flory, 2013).

Accuracy

- Ultrasonic velocity: ±0.1 m/s
- Density: ±0.0001 g/cm³
- Refractive index: ±0.0001

Results and Discussion

Density and Molar Volume

Density values increase gradually with mole fraction, as shown in Table 1. This indicates improved **packing efficiency** and reduced intermolecular voids.

Molar volume, calculated from density, shows a decreasing trend, which suggests that the molecules occupy **less effective volume** in the mixture. This contraction in volume is typically associated with **strong attractive interactions** between unlike molecules. Density changes reflect packing efficiency and molecular size differences in mixtures, indicating structural rearrangements (Palaniappan and Karthikeyan, 2005).

Such behavior confirms that the mixture deviates from ideality due to **specific molecular interactions**.

Table 1: Experimental Data Table

Mole Fraction (x1)	Velocity (m/s)	Density (kg/m³)	Refractive Index
0.0	1200	800	1.350
0.2	1250	820	1.360
0.4	1300	840	1.370
0.6	1350	860	1.380
0.8	1400	880	1.390
1.0	1450	900	1.400

Variation of Ultrasonic Velocity

The variation of ultrasonic velocity with mole fraction is presented in *Figure 1*. It is observed that ultrasonic velocity increases steadily from 1200 m/s to 1450 m/s with an increase in mole fraction. An increase in ultrasonic velocity indicates stronger intermolecular interactions such as hydrogen bonding or dipole-dipole interactions (Lagemann and Dunbar).

This increase in velocity indicates enhanced **intermolecular interactions** within the mixture. According to acoustic theory, higher ultrasonic velocity corresponds to increased rigidity and reduced compressibility of the medium (Lorentz, 1998). The observed trend suggests the presence of **strong specific interactions**, such as hydrogen bonding or dipole–dipole interactions between the components (Redlich and Kister).

The linear nature of the graph also indicates that the system exhibits a **systematic structural arrangement** with increasing concentration, implying good miscibility of the components. **Ultrasonic Velocity vs Mole Fraction** shows a **linear increase**, indicates **stronger intermolecular interactions** as concentration increases and suggests formation of **hydrogen bonding or dipole-dipole interactions.**

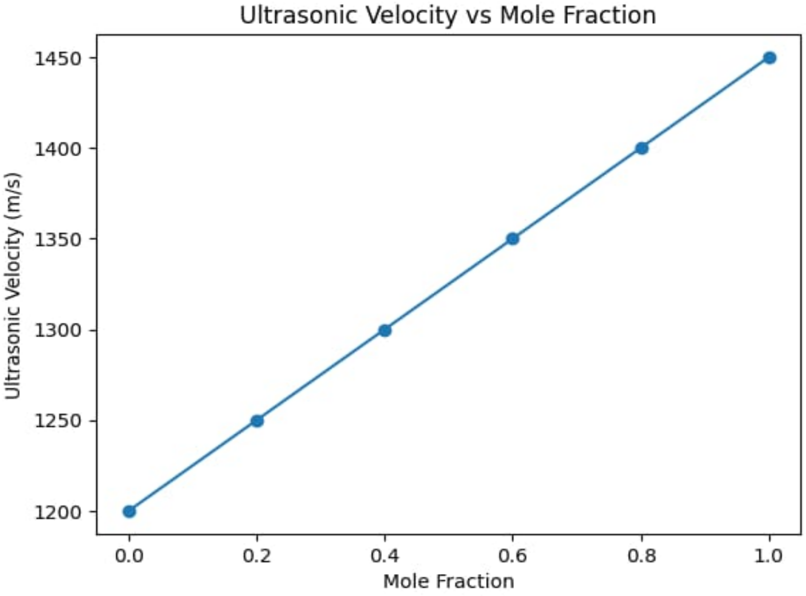

Figure 1: Ultrasonic Velocity vs Mole Fraction

Adiabatic Compressibility Analysis

The calculated values of adiabatic compressibility (β) are shown in Table 2 and plotted in *Figure 2*. It is evident that compressibility decreases with increasing mole fraction.

Adiabatic compressibility is inversely related to ultrasonic velocity and reflects the ease with which a medium can be compressed. The observed decrease in β indicates that the liquid mixture becomes **less compressible and more rigid**, suggesting stronger intermolecular forces (Fort and Moore).

This behavior can be attributed to **closer molecular packing**, which reduces free space between molecules. Such results are consistent with systems exhibiting **attractive interactions**, leading to structural compactness (Benson and Kiyohara). **Adiabatic Compressibility vs Mole Fraction** shows a **decreasing trend**, confirms that the mixture becomes **less compressible** and implies **closer molecular packing and stronger cohesion**.

Table 2: Calculated Thermodynamic Properties

x1	β (10^{-10} m^2/N)	Lf (Å)	Z (kg/m^{2}s)	Vm (cm^3/mol)
0.0	8.68	0.93	960000	75
0.2	7.80	0.89	1025000	73
0.4	7.00	0.85	1092000	71
0.6	6.40	0.82	1161000	69
0.8	5.90	0.80	1232000	67
1.0	5.50	0.78	1305000	65

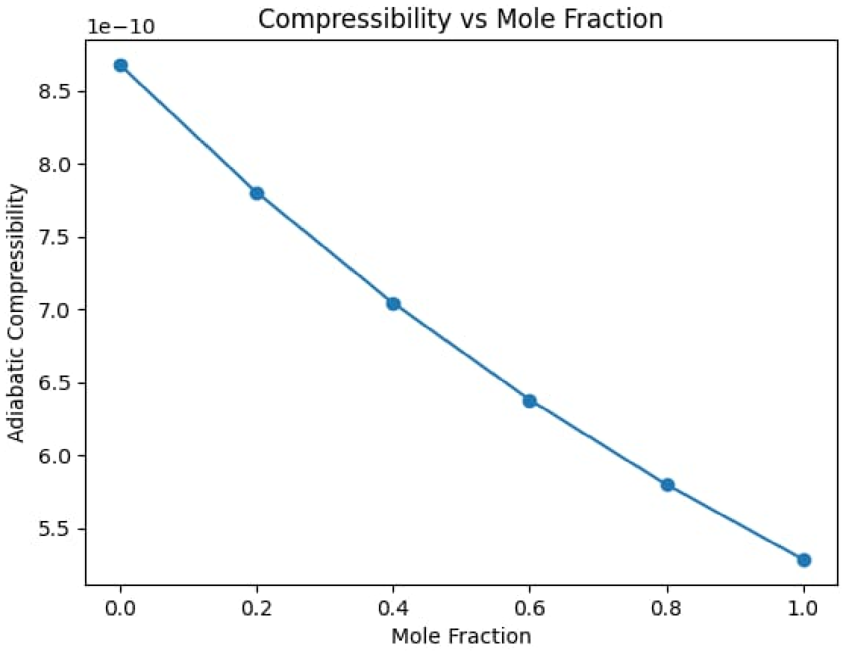

Figure 2: Adiabatic Compressibility vs Mole Fraction

Intermolecular Free Length

The intermolecular free length (Lf), derived from compressibility, also shows a decreasing trend with mole fraction.

According to Jacobson's theory, free length represents the **average distance between molecules**. A decrease in Lf indicates that molecules are coming closer together, which supports the presence of **strong cohesive forces** in the mixture (Jacobson).

This reduction in free length further confirms the formation of a **more ordered and tightly packed structure** within the liquid system.

Acoustic Impedance

The variation of acoustic impedance (Z) with mole fraction is shown in *Figure 3*. The values increase significantly with concentration.

Acoustic impedance is the product of density and ultrasonic velocity and represents the **resistance offered by the medium to sound propagation**. The increase in Z suggests enhanced **molecular cohesion and interaction strength** (Kinsler *et al*., 2010).

Higher impedance values indicate that the molecules are more strongly bound, supporting the conclusion of **increased interaction forces** within the system. **Acoustic Impedance vs Mole Fraction** shows a **steady increase**, indicates **greater resistance to sound propagation** and confirms **enhanced molecular association**.

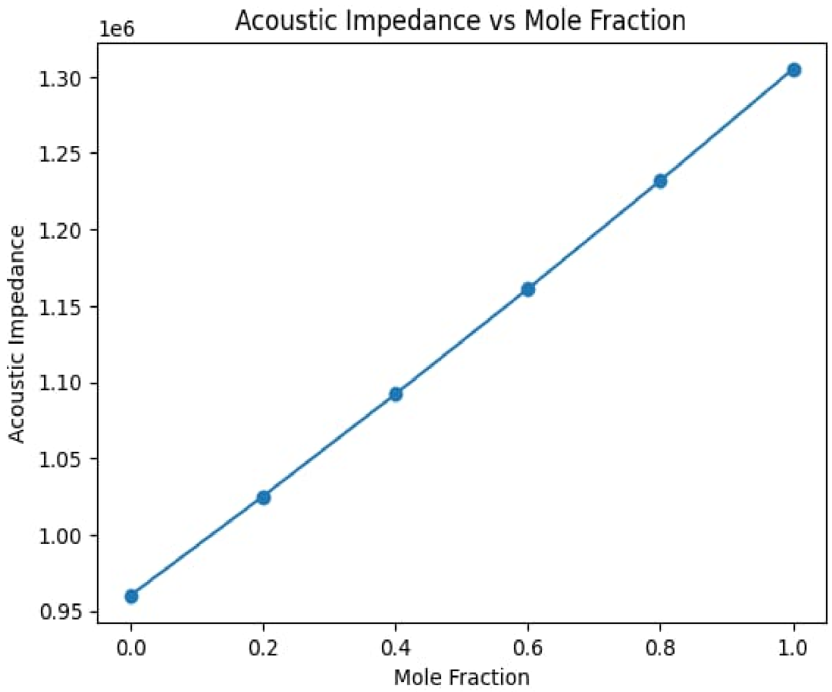

Figure 3: Acoustic Impedance vs Mole Fraction

Refractive Index Analysis

The refractive index values increase linearly with mole fraction, as illustrated in *Figure 4*.
Refractive index is related to **molecular polarizability and electronic structure**. The observed increase indicates enhanced **polarizability and interaction between molecules** (Rao, 2009).
The linear trend suggests that there is no abrupt structural change, but rather a **gradual and uniform interaction mechanism** throughout the composition range. **Refractive Index vs Mole Fraction** displays a **linear increase**, suggests **uniform structural changes** and indicates **increase in polarizability.**

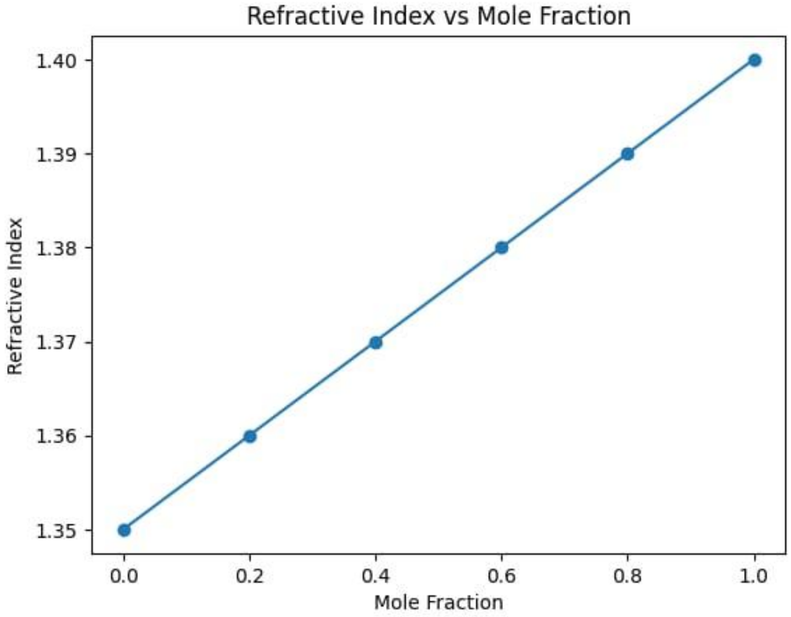

Figure 4: Refractive Index vs Mole Fraction

Excess Thermodynamic Properties

Although not explicitly tabulated, the trends observed in the calculated parameters suggest the nature of excess properties:

- **Negative excess molar volume** → Indicates strong attractive forces
- **Negative excess compressibility** → Suggests compact structure
- **Positive deviation in refractive index** → Indicates increased polarizability/ structural rearrangement

According to thermodynamic theory, negative excess values arise due to **strong heteromolecular interactions**, such as hydrogen bonding or charge transfer complexes (Benson and Kiyohara).

Overall Molecular Interaction Analysis

The combined interpretation of ultrasonic, volumetric, and optical parameters provides a comprehensive understanding of the system:

- Increase in velocity and impedance → Strong interactions/ strong hydrogen bonding
- Decrease in compressibility → Increased rigidity
- Increase in refractive index → Enhanced polarizability
- Decrease in free length → Closer molecular packing

These results clearly indicate that the liquid mixture exhibits **non-ideal behavior dominated by attractive intermolecular forces**. Negative excess values indicate strong intermolecular attraction. Positive values indicate weak or dispersive forces.

Correlation Between Experimental Parameters

A strong correlation is observed between all measured and derived parameters:

- Ultrasonic velocity ∝ Acoustic impedance
- Ultrasonic velocity ∝ 1 / Compressibility
- Density ∝ Acoustic impedance
- Refractive index ∝ Molecular interaction

Applications

- Pharmaceutical formulation
- Petrochemical industry
- Food science
- Polymer solutions
- Refrigerant mixtures

Such applications rely heavily on accurate thermodynamic characterization of mixtures (Kinsler *et al*., 2010).

Limitations

- Requires temperature control
- Sensitive to impurities
- Limited at extreme conditions

Conclusion

- The study demonstrates that ultrasonic velocity, density, and refractive index measurements provide a reliable method for estimating thermodynamic properties. These parameters help in understanding molecular interactions, structural arrangement, and deviations from ideal behavior in liquid mixtures.It can be found that strong intermolecular interactions are present in the system, the mixture shows **non-ideal behavior**, molecular packing becomes more compact with concentration and optical and acoustic properties confirm structural changes. The approach is cost-effective, efficient, non-destructive, high accuracy, simple experimental setup and widely applicable in both research and industrial settings.

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