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A Review on Molecular Interactions in Binary Liquid Mixtures Investigated by Ultrasonic Studies

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Abstract: ***Ultrasonic techniques is one of the most reliable and non-destructive methods for the investigation of molecular interactions in liquid mixtures. The propagation of ultrasonic waves through liquids is strongly influenced by intermolecular forces, making ultrasonic measurements valuable for understanding the structural and thermodynamic behavior of binary liquid mixtures. By measurement of ultrasonic velocity with density and viscosity measurements, several acoustical and thermodynamic parameters—including adiabatic compressibility, intermolecular free length, free volume, internal pressure, acoustic impedance, relaxation strength, and excess properties—can be evaluated. These parameters provides valuable information about the nature and strength of molecular interactions such as hydrogen bonding, dipole–dipole interactions, ion–dipole interactions, charge-transfer complexes, and dispersion forces. Numerous studies have demonstrated that deviations in acoustical parameters from ideal behavior reveal the extent of molecular association or dissociation in liquid mixtures. This review gives an idea about the theoretical principles of ultrasonic wave propagation, discusses the determination of important acoustical parameters, reviews ultrasonic investigations of binary liquid mixtures, and highlights applications of ultrasonic studies in chemistry and industrial processes. The article also discusses recent developments and future prospects for ultrasonic characterization of molecular interactions.***

Keywords: Ultrasonic velocity, Molecular interactions, Binary liquid mixtures, Acoustic impedance, Adiabatic compressibility, Intermolecular free length, Acoustic Parameters.

I. INTRODUCTION

The molecular interactions studies in liquid mixture is fundamental to understanding physicochemical processes such as solvation, diffusion, chemical reactivity, and phase equilibrium. Intermolecular forces are useful to illustrate structural arrangement and physical properties of liquid systems. Binary liquid mixtures, consisting of two chemically distinct components, provide excellent model systems for investigating these interactions because their composition can be varied continuously. Such mixtures are extensively employed in chemical industries, pharmaceuticals, coatings, fuels, and biological systems [1,2]. Among the several experimental techniques, ultrasonic measurements technique have gained widespread acceptance due to their simplicity, accuracy, rapidity, and non-destructive nature [3,4].

Ultrasonic waves with frequencies above 20 kHz when propagates through liquids, their velocity depends strongly on the elastic properties and molecular arrangement of the medium. Any change in intermolecular attraction alters the compressibility and density of the liquid, thereby affecting ultrasonic velocity [5,6]. Measurement of ultrasonic velocity along with density and viscosity, enable the calculation of numerous acoustical and thermodynamic parameters that provide valuable information regarding molecular interactions[7]. These include: Adiabatic compressibility, Intermolecular free length, Acoustic impedance, Free volume, Internal pressure, Relaxation time, Rao's constant, Wada's constant, Excess properties etc. The variation of these parameters with concentration and temperature helps identify the nature and strength of intermolecular interactions. Strong hydrogen bonding generally results in increased ultrasonic velocity and decreased adiabatic compressibility, whereas weak interactions often exhibit opposite trends[8]. The objective of this review is to summarize the theoretical background of ultrasonic studies, explain the interpretation of acoustical parameters, and review their application in understanding molecular interactions in binary liquid mixtures[9].

II. PRINCIPLE OF ULTRASONIC STUDIES

Ultrasonic waves are longitudinal pressure waves that propagate through liquids by successive compression and rarefaction of molecules. Since liquids cannot support shear stress, only

The ultrasonic velocity (**U**) is given by

$\mathbf{v = \lambda \times f,}$ Where v - Ultrasonic velocity, f - Frequency., λ - Wavelength

According to the Newton–Laplace equation,

III. CERTAIN ACOUSTICAL PARAMETERS USED IN MOLECULAR INTERACTION STUDIES

Several acoustical parameters are derived from experimental measurements.

A. *Adiabatic Compressibility*

$\beta_s = 1/v^2\rho_s$, Where v – Ultrasonic velocity, ρ – Density of solution. Units – m^2N^{-1}

When molecules interact strongly through hydrogen bonding or dipole interactions, the liquid becomes less compressible, leading to higher ultrasonic velocity.

Lower compressibility indicates stronger intermolecular attraction and closer molecular packing[10].

B. *Intermolecular Free Length*

Jacobson related free length to compressibility by

$L_f = K\sqrt{\beta_S}$ where **K** is Jacobson's temperature-dependent constant.

A decrease in free length indicates stronger molecular association [11].

C. *Acoustic Impedance*

Z = v . ρs Acoustic impedance increases with stronger molecular interactions because both density and ultrasonic velocity generally increase [12].

D. *Free Volume*

Free volume reflects the available space for molecular movement. Strong intermolecular attraction decreases free volume because molecules become more closely packed [13].

E. *Internal Pressure*

Internal pressure represents cohesive forces acting within liquids. Higher internal pressure generally indicates stronger molecular association arising from hydrogen bonding or dipole interactions[14].

IV. EXCESS ACOUSTICAL AND THERMODYNAMIC PARAMETERS

While absolute acoustical parameters provide valuable information about liquid structure, **excess properties** are more sensitive indicators of molecular interactions because they quantify deviations from ideal mixing behavior. Excess functions arise from differences in molecular size, shape, polarity, and intermolecular forces between the components of a binary liquid mixture[15]. The most frequently reported excess parameters in ultrasonic investigations include: Excess ultrasonic velocity, Excess adiabatic compressibility, Excess intermolecular free length , Excess molar volume, Excess acoustic impedance, Excess viscosity, Excess Gibbs free energy of activation etc. Negative values of excess compressibility or free length generally indicate stronger attractive interactions such as hydrogen bonding or dipole–dipole association. Positive deviations often suggest weaker interactions, structural disruption, or steric effects [15, 16].

V. TYPES OF MOLECULAR INTERACTIONS IN BINARY LIQUID MIXTURES

The properties of binary liquid mixtures are governed by the nature and strength of intermolecular forces. Ultrasonic studies are particularly effective in distinguishing among these interactions like - Hydrogen Bonding, Dipole–Dipole Interactions, Dipole–Induced Dipole Interactions, Dispersion (London) Forces, Charge-Transfer Complex Formation etc.

VI. APPLICATIONS OF ULTRASONIC STUDIES :

Ultrasonic investigations of molecular interactions have broad applications across science and industry.

1) Chemical Industry: Ultrasonic measurements assist in understanding solvent–solute interactions, optimizing solvent selection, and monitoring reaction progress with reference to the use of various solvents.
2) Pharmaceutical Sciences: The Ultrasonic technique is used the study of drug solubility, formulation stability, and excipient compatibility for binary and multicomponent liquid systems[17].
3) Petrochemical Industry: Ultrasonic techniques are used for quality assessment of fuels, lubricants, and petroleum fractions by correlating acoustic parameters with composition.

4) Food and Beverage Industry: Ultrasonic methods enable rapid, non-destructive evaluation of edible oils, alcoholic beverages, fruit juices, and dairy products through measurements related to density and compressibility[18].

5) Materials Science: Ultrasonic characterization is applied to polymers, nanofluids, ionic liquids, and advanced functional materials to investigate molecular organization and intermolecular interactions.

VII. RECENT ADVANCES IN ULTRASONIC STUDIES OF MOLECULAR INTERACTIONS

Recent developments in ultrasonic instrumentation and computational chemistry have significantly enhanced the study of molecular interactions in liquid mixtures. High-precision digital ultrasonic interferometers operating at frequencies between 1 and 10 MHz provide accurate measurements of ultrasonic velocity with minimal experimental uncertainty. By the use of automated digital density meters, Thermostat and viscometers, these instruments enable reliable determination of acoustical and thermodynamic parameters over wide range of temperature and concentration. The integration of ultrasonic measurements with spectroscopic techniques, such as Fourier Transform Infrared (FTIR), Raman spectroscopy, Nuclear Magnetic Resonance (NMR), and UV–Visible spectroscopy, has improved the interpretation of intermolecular interactions. While ultrasonic methods provide indirect evidence through changes in acoustic properties, spectroscopic techniques identify specific functional groups involved in hydrogen bonding or complex formation[19]. Computational approaches have also become increasingly important. Molecular dynamics (MD) simulations and quantum chemical calculations are now widely used to correlate experimentally determined acoustic parameters with microscopic structural features. These methods help explain hydrogen-bond networks, dipole orientations, and molecular packing in binary liquid mixtures [20]. Such combined experimental and computational studies provide a more complete understanding of liquid structure than either approach alone. Interest has also grown in applying ultrasonic techniques to ionic liquids, deep eutectic solvents, biofuels, nanofluids, and environmentally benign ("green") solvents. These systems are relevant to sustainable chemistry and advanced industrial applications, where knowledge of molecular interactions is essential for process optimization[21].

VIII. FUTURE PERSPECTIVES

Ultrasonic investigations are expected to remain an important tool for studying molecular interactions because they are non-destructive, rapid, and relatively inexpensive. Future research is likely to focus on: Multicomponent liquid mixtures with industrial relevance, Environmentally friendly solvent systems and green chemistry, Pharmaceutical formulations requiring precise characterization of molecular interactions, Nanofluids and colloidal systems with tailored physicochemical properties, Integration of ultrasonic measurements with artificial intelligence and machine learning for predicting thermodynamic behavior, Simultaneous use of ultrasonic, spectroscopic, and computational techniques to obtain a comprehensive molecular-level understanding. Standardization of experimental procedures, uncertainty analysis, and reporting practices will improve the comparability of results obtained by different laboratories.

IX. CONCLUSION

Ultrasonic studies have become one of the most effective methods for investigating molecular interactions in binary liquid mixtures. Measurements of ultrasonic velocity and associated parameters together, allow the calculation of important acoustical and thermodynamic parameters. These parameters provide valuable information regarding the strength and nature of intermolecular forces, including hydrogen bonding, dipole–dipole interactions, dipole-induced dipole interactions, and London dispersion forces. The variations in the values of excess acoustical properties has proven particularly useful for distinguishing ideal and non-ideal mixing behavior. Negative excess compressibility and free length generally indicate strong attractive interactions and molecular association, whereas positive deviations often reflect weaker interactions or structural disruption. Studies of binary mixtures containing alcohols, ketones, amides, sulfoxides, aromatic hydrocarbons, and water have demonstrated the versatility of ultrasonic techniques in characterizing liquid structure over a wide range of compositions and temperatures.

Recent advances in instrumentation, molecular simulation, and complementary spectroscopic techniques have expanded the scope of ultrasonic investigations. As new solvent systems, pharmaceutical formulations, ionic liquids, and sustainable chemical processes continue to emerge, ultrasonic characterization is expected to play an increasingly important role in understanding molecular organization and predicting physicochemical behavior.

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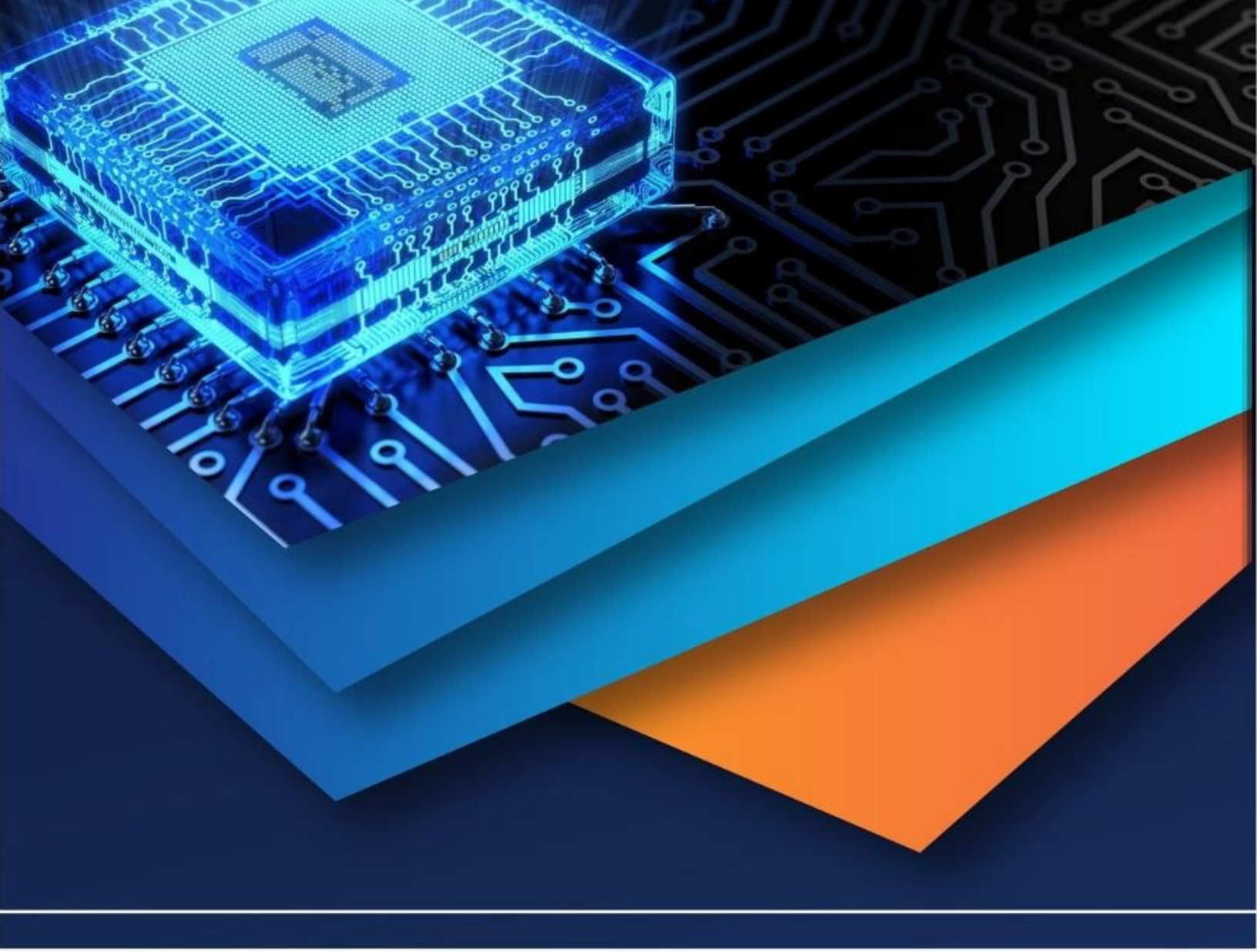

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