Vidyabharati International Interdisciplinary Research Journal
ISSN 2319-4979

Ultrasonic Interferometric Technique for Molecular Interaction Studies of Liquid Mixtures : A Review

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Abstract
To understand the structural, thermodynamic, and physicochemical behavior of multicomponent systems, The study of molecular interactions in liquid mixtures is important. For liquid mixtures formed by dissolving solute in solvents, behavior of liquid mixtures is depend on solubility. Therefore one can say in pharmacology about drugs "compounds with insufficient solubility carry a higher risk of failure. For such mixtures, ultrasonic interferometry is a sensitive, non-destructive experimental technique widely employed to investigate such interactions through the measurement of ultrasonic velocity in liquids and liquid mixtures. When ultrasonic velocity measurements are combined with density and viscosity data, several acoustic, thermodynamic, and excess parameters can be evaluated. These include adiabatic compressibility, acoustic impedance, intermolecular free length, relaxation time, free volume, internal pressure, excess molar volume, excess compressibility, excess ultrasonic velocity, and excess free energy. The magnitude and sign of these parameters provide useful information concerning molecular association, dissociation, hydrogen bonding, dipole–dipole interactions, dipole-induced interactions, charge-transfer interactions, and structural changes occurring upon mixing. This review summarizes the principle of ultrasonic interferometry, experimental methodology, important acoustic and thermodynamic parameters, and their interpretation in terms of molecular interactions.

Keywords: *Ultrasonic interferometry; liquid mixtures; molecular interaction; ultrasonic velocity; adiabatic compressibility; excess properties; intermolecular free length; thermodynamic properties; hydrogen bonding.*

Introduction

Several experimental techniques are employed to investigate the properties of condensed phase system such as pure and mixed liquid phase system. The nature and strength of the bonds present that is molecular interactions in a given liquid system are probed using the experimental techniques like thermodynamic, transport, spectroscopic, dielectric NMR, UV, Visible, microwave etc. the study of molecular interactions in the liquid mixtures is very much important to study the structural properties of molecules. Ultrasonic energy is used in medicine, engineering, agriculture, defense and industry. In chemical industries, ultrasonic energy is found useful in studying the chemical processes and in synthesis of chemical substances. In solution of ionic solute, the attraction between the solute and solvent is of ion-dipole type, when electrolyte is dissolved in solvent, it causes volume contraction due to interaction between ions and solvent molecules and therefore other acoustical parameters may be affected. Many researchers have used ultrasound to investigate the ion-solvent interactions in aqueous solutions containing electrolytes[1-7]. A survey of literature[8-9]reveals that ultrasonic waves with low amplitude suggesting weak ion-solvent interactions and have been used by many scientists to investigate the nature of molecular interactions and physicochemical behaviors of pure, binary liquid mixtures

Liquid mixtures are encountered extensively in chemical processing, pharmaceutical formulations, fuels, solvents, separation processes, heat-transfer systems, and many other technological applications. Their macroscopic properties are strongly influenced by molecular interactions between the constituent components. Consequently, understanding the nature and strength of interactions in binary, ternary, and multicomponent liquids is an important problem in physical chemistry and chemical physics[10].

Molecular interactions in a liquid mixture can involve solvent–solvent, solute–solute, and solute–solvent interactions. On mixing two liquids, the original molecular associations may be weakened, strengthened, or replaced by new interactions between unlike molecules. These changes can produce significant deviations from ideal behavior. Hydrogen bonding, dipole–dipole attraction, dipole-induced dipole interactions, dispersion forces, steric effects, charge-transfer interactions, and molecular association are among the mechanisms frequently responsible for such deviations.

Ultrasonic techniques have become important tools for investigating these phenomena because ultrasonic propagation is sensitive to the elastic and structural properties of the medium. In

particular, ultrasonic interferometry allows the velocity of sound through a liquid to be determined accurately. Measurements of ultrasonic velocity can subsequently be combined with density and viscosity measurements to obtain a range of acoustic and thermodynamic properties. Recent reviews have emphasized the usefulness of these techniques for investigating binary and ternary liquid systems and their molecular interactions[11].

The ultrasonic velocity of a liquid is related to its compressibility and density. Therefore, changes in velocity with composition and temperature provide information about changes in molecular packing and intermolecular forces. The deviation of experimental properties from ideal or theoretical values is particularly useful for interpreting molecular interactions.

Principle of Ultrasonic Interferometry:

It is the branch of physical chemistry concerned with ultrasonic wave. It is defined as the vibrations of frequencies greater than the upper limit of the audible range for humans that are greater than about 20 KHz. The term sonic is applied to ultrasound waves of very high frequencies. Hyper sound, sometimes called sound or micro sound is sound waves or frequencies greater than 10^{13} Hertz.

Ultrasonic wave propagation in liquid has been the subjects of exhaustive research which has been carried out theoretically and practically. When solute is dissolved in solvent, there is interaction which takes place either in between solute –solvent molecules or solvent-solvent molecules. There has been large number of studies done on the molecular interaction in liquid system. There are many approaches and spectroscopic techniques used to determine the structure-function relation of molecules.Among the techniques used, ultrasonic velocity measurements through liquid medium gain much more importance in assessing the nature of molecular interactions[12].

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

Densities of liquids are measured by various methods that are by weighing a definite volume of liquid in a specific gravity bottle or using pyknometer. Anton paar DMA - 35 is the digital density meter and it is portable device which gives direct readings of density with accuracy of $0.001 g/cm^3$ and at different temperatures.By using Ostwald's viscometer, relative viscosity can be measured accurately with respect to say water. In the present investigation, ostwald's viscometer is used to measure the viscosities of pure liquid and liquid mixtures.

Commercial interferometers frequently operate at frequencies around 1–5 MHz. Several published studies, for example, have used a 2 MHz ultrasonic interferometer for binary liquid mixtures.The temperature of the sample must be controlled carefully because ultrasonic velocity is strongly temperature dependent.

Acoustic and Thermodynamic Parameters :

In the recent years, the thermo-acoustic parameters are of considerable importance in understanding the intermolecular reactions in binary mixtures. Ultrasonic technique is used in the study of nature and extent of patterns of molecular aggregations that exists in liquid mixtures resulting from intermolecular interactions[13].

The various empirical relations are used to derive acoustic and thermodynamic parameters discussed below.

Adiabatic Compressibility (β_s) :$\mathbf{\beta_s = 1/ v^2\rho_s}$ **,** Where v – Ultrasonic velocity

ρ – Density of solution, Units – m^2N^{-1}

The increase in adiabatic compressibility may be due to departure of solvent interactions. When salvation process is in progress, solvent molecule separates the solute molecule with increase in mobility. In such case, adiabatic compressibility should decrease on dilution.According to Jacobson, by the value of K[13], intermolecular free length (Lf) can be given by the formula – $\mathbf{L_f = K\sqrt{\beta_S}}$ .Specific acoustic impedance is the measures of the opposition that a system presents to the acoustic flow resulting of an acoustic pressure applied to the system. It is denoted by Z. It is a product of ultrasonic velocity (v) and density (ρ)

$\mathbf{Z = v .\rho_s}$**,**ρ_s– density of the solution**,** v – Ultrasonic velocity of liquid medium.

Relative association is the measure of extent of association of components in the medium. When the solute is added to the solvent, salvation of solute particles takes place. It is denoted by RA.R_A= ρs /ρo [vo / vs]1/3

Unit-DimentionlessRelaxation Time (τ) :It is the characteristic time in which a system relaxes under certain changes in external conditions. It is calculated by using equation,

$\tau = 4/3\ \beta s \times \eta$, Relaxation time is the time taken for the excitation energy to appear as translational energy and depends on temperature and on impurities.In the liquid medium, the molecules are not quiet closely packed and there is some free space between the molecules for movement, the free space that volume is called as free volume. Eyring and Kincaid defined the free volume (Vf) is the effective volume in which particular molecule of the liquid can move and obey perfect gas laws.It is given by the equation.$Vf = (Meff \times vs / k \times \eta)3/2$

Molar sound velocity is called as Rao's constant. It is calculated by using the equation,

$R = (Meff / \rho S) \times v1/3$, Wada's constant also termed as molar compressibility.

It is calculated by the equation $-W = (Meff/\rho S) \times \beta\ -1/7$

An apparent molar property of a solution component in a mixture or solution is a quantity defined with the purpose of isolating the contribution of each component to the non ideality of the mixtures. It is defined as apparent because it appears to represent the molar property of that component in solution. The different apparent molar properties that are commonly used, one such apparent molar property is apparent molar compressibility (Φk).

It is given by equation-$\Phi k = [1000\ (\beta s d_0 - \beta_0 ds) / m\ ds d_0] + (\beta s\ M/ds)$

Electrolytic Conductance is defined as the conducting power of all the ions produced by disoolving one gram mole of an electrolyte in solution. Conductivity of the solution is depends on the presence in the solution and also depends on the polar nature of the solute. It is calculated by relation.Equivalent Conductance - $\lambda m = Kc\ [1000/N]$

Interpretation of Molecular Interactions :

When unlike molecules interact more strongly than like molecules, the mixture may show strong association.Typical examples include:Hydrogen bonding,Dipole–dipole attraction,Ion–dipole interaction,Charge-transfer interaction.Such interactions can result in closer molecular packing and significant deviations in acoustic and thermodynamic properties.

For example, studies involving N-methyl-2-pyrrolidone and aliphatic esters reported strong interactions based on the composition and temperature dependence of excess thermodynamic properties.

Hydrogen Bonding :

Hydrogen bonding is particularly important in mixtures containing alcohols, amines, carboxylic acids, water, and other hydrogen-bonding molecules.

An alcohol molecule may form an extensive self-associated hydrogen-bond network. When another component is introduced, the original alcohol–alcohol association can be disrupted and replaced by alcohol–solute interactions.

Thus, ultrasonic measurements can provide indirect evidence of:

Type of Interactions :

Studies of alcohol-containing mixtures have frequently interpreted ultrasonic and excess properties in terms of hydrogen-bond disruption and formation of new unlike-molecule associations.

Dipole–Dipole Interactions:

Polar molecules possess permanent electric dipole moments. When two polar molecules interact, their orientation may lead to attractive dipole–dipole forces.Such interactions can affect:-Ultrasonic velocity, Adiabatic ompressibility,density,viscosity,free length, excess volum etc.

Dipole-Induced Dipole Interactions:

A polar molecule can induce a temporary dipole in a non-polar molecule. Such interactions may become important in mixtures containing polar and non-polar components.

Charge-Transfer Interactions :

Charge-transfer complexes can form when an electron donor interacts with an electron acceptor.Ultrasonic measurements can be combined with spectroscopic methods to investigate such complexes. In ternary systems containing iodine and aromatic or heterocyclic donor molecules, acoustic excess parameters have been used alongside optical measurements to investigate charge-transfer-complex formation.

Effect of Temperature : Temperature strongly influences ultrasonic and thermodynamic properties.With increasing temperature:Molecular thermal motion increases, Intermolecular

association may weaken, Density generally decreases, Viscosity generally decreases, Free volume may increase,Ultrasonic velocity may change depending on the balance between density and compressibility effects.Consequently, molecular-interaction studies should preferably be performed at several temperatures when the objective is to understand the temperature dependence of association.

Applications of Ultrasonic Interferometry :

Ultrasonic molecular-interaction studies have applications in several fields:

Ultrasonic and thermodynamic data are useful for understanding fluid behavior in:Separation processes, Solvent extraction, Distillation, Heat transfer, Mass transfer,Process design.Thermophysical properties of multicomponent fluids are particularly important in industrial process calculations.Ultrasonic methods can be used to investigate solute–solvent interactions, drug–solvent interactions, and molecular association in solution[14].Ultrasonic techniques can characterize interactions in polymer solutions, nanofluids, and other complex liquid systems.The method can be applied to aqueous and mixed-solvent systems relevant to biochemical and environmental chemistry.Ultrasonic measurements provide information about molecular packing, association, structural changes, and non-ideal solution behavior.

The major advantages include: It is non-destructive technique, The liquid sample is not chemically altered during measurement, Relatively small quantities of liquid can be studied.

The measurements are carried out quickly. The technique is highly sensitive. Small changes in molecular structure can influence acoustic properties. The technique has wide applicability like binary, ternary, polymeric, electrolyte, and other liquid systems can be studied.Measurements can be performed at different controlled temperatures. Ultrasonic measurements can be combined with density, viscosity, spectroscopy, and computational approaches.Recent reviews identify the non-destructive nature and sensitivity of ultrasonic methods as important reasons for their continued use in liquid-mixture research.

Limitations :

Despite its advantages, ultrasonic interferometry has some limitations like ultrasonic velocity does not directly identify a particular molecular bond. Molecular-interaction conclusions are inferred from combinations of acoustic and thermodynamic parameters.Small temperature variations can produce measurable changes in velocity, density, and viscosity. Accurate temperature control is therefore essential. Some experimental errors may arises like uncertainty in reflector displacement,frequency stability,temperature fluctuations,sample impurities,evaporation,air bubbles,calibration errors.Mechanical limitations such as nonlinear thread motion, backlash, and difficulties in controlling transducer separation have also been identified for variable-path ultrasonic interferometers.

Need for Complementary Techniques :

For definitive identification of molecular structures or complexes, ultrasonic measurements are preferably combined with techniques such as FTIR, Raman spectroscopy, NMR, dielectric measurements, molecular dynamics simulations, or quantum-chemical calculations.

Future Perspectives :

Future research can improve the molecular interpretation of ultrasonic measurements by combining experimental acoustics with modern computational and spectroscopic techniques.Ultrasonic measurements combined with FTIR and Raman spectroscopy, Molecular dynamics simulations of liquid mixtures, Machine-learning analysis of acoustic and thermodynamic datasets, High-pressure ultrasonic measurements, Nanofluid and polymer-solution investigations, Simultaneous ultrasonic, Density, Viscosity, and Dielectric measurements;Investigation of multicomponent and ionic liquid systems.Such combined approaches can help distinguish whether observed acoustic deviations originate primarily from hydrogen bonding, molecular packing, size effects, dipolar interactions, or other structural changes.

Conclusion :

Ultrasonic interferometry is an effective experimental technique for investigating the physicochemical behavior of liquid mixtures. Measurement of ultrasonic velocity, when combined with density and viscosity, allows numerous acoustic and thermodynamic properties to be evaluated. The composition and temperature dependence of these properties provides

indirect but valuable information about molecular association, dissociation, hydrogen bonding, dipole–dipole interactions, dipole-induced interactions, charge-transfer interactions, and changes in molecular packing.Excess properties are especially useful because they quantify deviations from ideal behavior. However, no single acoustic parameter should generally be used as the sole basis for assigning a molecular interaction. A reliable interpretation requires simultaneous consideration of ultrasonic velocity, density, viscosity, excess properties, molecular structure, temperature dependence, and, where possible, independent spectroscopic or computational evidence.

Overall, ultrasonic interferometry remains a useful and relatively simple method for investigating molecular interactions in binary and multicomponent liquid systems. Recent reviews confirm its continuing importance in studies of liquid mixtures and thermophysical properties.

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