

Study of Various Thermo-Acoustical Properties of Different Solvents

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Abstract: A study of the ultrasonic interferometer was conducted at room temperature and at 2 MHz, 4 MHz, and 6 MHz to look at the dynamical characteristics of various liquids. In terms of structural dynamics, inter- and intermolecular H-bonding, and intermolecular forces between solute and solvent molecules, acoustic parameters like ultrasonic velocity (v), compressibility (β), free length (L_f), acoustic impedance (Z), Rao's constant (R), and Wada's constant (W) have been discussed.

Keywords: Available volume, Adiabatic Compressibility, Gibb's Free Energy, Acoustic Impedance..

I. INTRODUCTION

Thermophysical, thermodynamic, and ultrasonic In order to fully understand inter- and intramolecular interactions, structural and physiochemical behavior, and to confirm different liquid states, properties of liquid mixes are of utmost importance. Many theories have made an effort to predict the characteristics of liquid mixes. To precisely measure the sound velocity in liquids, a systematic study of the thermodynamic parameters of solutions is conducted using a new form of multi-frequency ultrasonic interferometer.

The movement of a reflector changes the path length in the cell, and the electrical response of the cell to the oscillator is used to set the position of the standing wave at a standard frequency. The locations of these standing waves are then detected using an appropriate cathetometer. An examination of the potential alteration of mixtures' thermodynamic properties.

Ultrasonic sound refers to sound pressure with a frequency greater than the human audible range (20Hz to 20 KHz). When an ultrasonic wave propagates through a Medium, the molecules in that medium vibrate over very short distance in a direction parallel to the longitudinal Wave. During this vibration, momentum is transferred among molecules. This causes the wave to pass through the medium (Fig. 1).

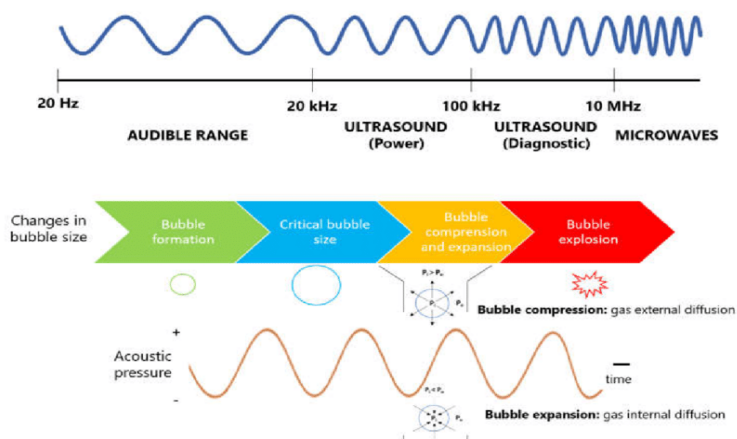


Fig. 1: Ultrasonic wave propagates through a medium

Interferometers are investigative tools used in many fields of science and engineering. They are called Interferometers because they work by merging two or more sources of light to create an interference pattern, which can be measured and analyzed; hence 'Interferometer'. The interference patterns generated by Interferometers contain information about the object or phenomenon being studied. They are often used to make very small measurements that are not

achievable any other way. The Michelson interferometer was used in 1887 in “Michelson-Morley experiment”, which set out to prove or disprove the existence of “Luminiferous Ether” a substance at a time thought to permeate the universe. All modern interferometers have evolved from this first one since it demonstrated how the properties of light can be used to make the tiniest of measurements. The invention of lasers has enabled interferometers to make the smallest conceivable measurements, like those required by LIGO. In short, ultrasonic interferometer is a simple device which yields accurate and consistent data, from which one can determine the velocity of ultrasonic sound in a liquid medium.

II. MATERIALS AND METHODS

Principle of Ultrasonic Interferometer

An Ultrasonic Interferometer is a simple and direct device to determine the Ultrasonic velocity in liquids with high degree of accuracy. The principle used in the measurement of velocity (v) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by a moveable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator becomes a maximum.

If the distance is now increased or decreased and if the variations are exactly one-half wavelengths ($\lambda/2$) or multiple of it, anode current becomes maximum.

The Instrument

The Ultrasonic Interferometer consists of the following parts: The High Frequency Generator: 2, 4 and 6 MHz, the Measuring Cell: 10 ml, base to hold the Cell and Coaxial cable.

The High Frequency Generator is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the “Measuring Cell”. A micrometer is provided to observe the changes in current and two controls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the High Frequency Generator. The Measuring Cell is specially designed double walled cell for maintaining the temperature of the liquid constant during the experiment. A fine micrometer screw has been provided at the top, which can lower or raise the reflector plate in the liquid in the cell through a known distance. It has a quartz crystal fixed at its bottom. In Multi-frequency Ultrasonic Interferometer Model MX-3, frequency selector knob should be positioned at desired frequency. It has single cell 1 MHz operating at fundamental frequency (2 MHz) and odd harmonics (4 and 6 MHz). For initial adjustment two knobs are provided on high frequency generator, one is marked with “ADJ” to adjust the position of the needle on the Ammeter and the knob marked “GAIN” is used to increase the sensitivity of the instrument for a greater deflection if desired. The ammeter is used to notice the number of maximum deflections while micrometer is moved up and down in the liquid as described in “Measurement” of the instruction manual.

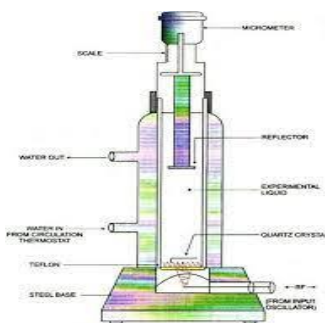


Fig. 2: Schematic Diagram of an Ultrasonic Interferometer.

III. EXPERIMENTAL METHODS

Adjust the cell's knurled cap and lift the cap away from the cell's double-walled construction. Pour the test substance into the center of it, then screw on the knurled cap. Wipe away any extra liquid that has overflowed into the cell. Place

the cell into the large base socket and secure it with the screw that is located on its side. Utilize the coaxial connection included with the instrument to connect the high frequency generator to the cell. Using the frequency choosing knob, choose the appropriate frequency. Move the micrometer slowly in either clockwise or anticlockwise direction till the anode current on the ammeter on the high frequency generator shows a maximum or minimum. Note the readings of micrometer corresponding to the maximum or minimum (whichever is sharper) in micrometer.

IV. RESULTS AND DISCUSSION

Below is a discussion of many ultrasonic parameters that need to be researched. Theoretical background information and the formulas to be applied in their calculation are provided in the discussion.

The ultrasonic velocity was determined by various methods by various researchers. The ultrasonic velocity determined by interferometer method is considered as more reliable and precise as compared to other methods have been reported in the literature for computing ultrasonic velocity. The velocity of ultrasonic waves in the liquid mixture have been measured using an ultrasonic interferometer (model MX-3, Mittal enterprises, New Delhi) working at a fixed frequencies of 2, 4 & 6 MHz in this instrument, using this instrument the wavelength (λ) of the ultrasonic wave in liquid and liquid mixtures can be determined. The expression used to determine the ultrasonic velocity is given by,

$$U = n \lambda \text{ ms}^{-1}$$

Where, 'n' is the frequency of the generator which is used to excite the crystal. In the present investigation, a constant frequency interferometer was employed & hence 'n' value is 1×10^6 Hz.

Adiabatic compressibility determines the orientation of the solvent molecules around the solute molecules. The structural change of the molecules in the mixture takes place due to the existence of electrostatic field between the interacting molecules. The structural arrangement of the molecule affects the adiabatic compressibility. It is the fractional decrease of volume per unit increase of pressure when no heat flows in or out.

These changes are related to the compressibility of the medium by thermodynamic relation,

$$\beta_a = 1/V * \delta v / \delta p]$$

Adiabatic compressibility is a measure of intermolecular association or repulsion. Singh and Kalsh showed that the adiabatic compressibility should be independent of temperature and pressure for unassociated and weakly associated molecules. It can also be calculated from the speed of sound (U) and the density of the medium (ρ) using the equation of Newton Laplace as,

$$\beta_a = (U^2 \rho)^{-1} \text{ Pa}^{-1}$$

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighboring molecules. Generally, when the ultrasonic velocity increases, the value of free length decreases. The decrease in intermolecular free length indicates the interaction between the solute and solvent molecules due to which the structural arrangement in the neighborhood of constituent ions or molecules gets affected considerably.

Acoustic impedance is important in the determination of acoustic transmission and reflection at the boundary of two materials having different acoustic impedance. It is also useful in the designing of ultrasonic transducers and for assessing absorption of sound in a medium. Mathematical relations for specific acoustic impedance (Z) and adiabatic compressibility (β_a) show that their behavior is opposite. According to Eyring and Kinacid, the free volume is the effective volume, in which the molecules in the liquid can move and obey perfect gas law. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions, which may occur when two or more liquids are mixed together.

Free volume is a very important factor in explaining the variations in the physicochemical properties of liquids and liquid mixture. Free volume is defined as the average volume in which the center of the molecules can move inside the hypothetical cell due to the repulsion of surrounding molecules. These molecules' interactions between like and unlike molecules are influenced by structural arrangements along with shape with shape and size of the molecules.

A liquid may be treated as composed of individual molecules each moving in a volume V_f in an average potential due to its neighbors. The molecules of a liquid are not quite closely packed and there is some free space between the molecules for movement and the volume V_f is called the free volume. Free volume can be calculated by different methods. Chellaiah et al, Eyring et al, Kinacid et al have made few approaches in calculating the free volume. Suryanarayana

and Kuppusamy on the basis of dimensional analysis, obtained an expression for free volume in terms of experimentally measurable parameters like ultrasonic velocity (U) and viscosity (η)

The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules. Cohesion creates a pressure within the liquid of value between 103 and 104 atmospheres. Internal pressure also gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interaction with the solvent arises through hydrogen bonding, charge transfer, columbic (or) Van der Waal's interaction. The term a/v^2 in Van der Waal's equation being the measure of attractive force of the molecule is called the cohesive (or) internal pressure. The internal pressure of the liquid mixture is obtained from the experimental values of ultrasonic velocity, density and viscosity using the relation,

$$\pi_i = bRT (\eta K/U)^{1/2} (\rho^{2/3} / M_{eff})^{7/6}$$

where, ρ is the density of liquid and KT is the temperature dependent constant having a value 205.8336×10^{-8} in MKS system at 298 K, K is constant equal to 4.28×10^9 in MKS system, b is a cubical packing fraction taken as 2 for all the liquids, R is the universal gas constant, T is the experimental temperature.

V. CONCLUSION

The discussed acoustical parameters (and their variations with molar concentrations and frequency) of any given solution of mixture of two or more different liquids provide useful information about the nature of intermolecular forces existing in the mixture. The existence of solvent-solvent interaction resulting in attractive forces promote the structure-making tendency, while solute-solute interaction resulting dipole-dipole, dipole induced dipole and electrostatic forces enhance the structure-breaking properties of given solution. It is obvious that the measurement of ultrasonic velocity in the provided medium serves as a useful probe in assessing the physical-chemical properties of the medium given the considerable existence of solute-solvent and solute-solute interactions present in the system to variable degrees.

These excess parameters have been used to discuss the nature and extent of interaction between the component molecules in the binary mixtures.

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