CHAPTER ~ 1
CHAPTER - 1

INTRODUCTION

1.1. ULTRASONICS

Ultrasonics deals with the study and application of sound waves having frequencies higher than 20,000 Hz which human ear can not respond and these frequencies are beyond the audible limit. The sound waves of frequency lower than the audible limits are called infra-sonics. Supersonics refers to the velocities higher than the velocity of sound, that is more than 1200 km/hour. Ultrasonic frequencies are used due to the following advantages.

1. Shorter wavelengths occur at higher frequencies, so that plain wave conditions are more easily realised which is especially important for the small specimens.

2. Absorption coefficients are usually much higher and easily measurable at higher frequencies.

3. Frequencies associated with relaxation phenomena often fall within the ultrasonic range and can be easily focused.

One of the notable applications of ultrasonic was in 1883 when Galton devised a high-frequency whistle to measure the upper frequency limit of response of human ear. Even at this time both the piezoelectric and magnetostrictive effects were known, but it was not until a sufficient degree of progress was made in the study of electronics that they could be used for the generation of ultrasonics.
Langevin made the first important use of ultrasonics during 1914-1918 war for underwater soundings. From then on, slow but steady progress was made in the measurements of propagation constants of materials. Early landmarks included Pierce’s quartz-driven ultrasonic interferometer in 1925\(^1\) and the discovery in 1932 by Debye and Sears and also by Lucas and Biquard of the ultrasonic diffraction grating. Pierce’s observations of velocity dispersion in carbon dioxide and work done in 1928 by Herzfeld and Rice on thermal relaxation showed that ultrasonic measurements could produce valuable information about the physical properties of the metals in which the waves were propagated. An important event during 1930s was the pioneering work of Sokolov in 1934 on ultrasonic flaw detection.

It was not until end of second world war that any major advances were made in ultrasonics. The discovery of radar led to the development of the pulse technique and its applications to the non-destructive testing of materials and to medical diagnoses. At the same time considerable advances were made in the application of ultrasonics in the various fields. Some of them are given in fig.1.1.

1.2. PRODUCTION OF ULTRASONIC WAVES

Ultrasonic waves can be produced by the following methods\(^2\).

- Galton Whistle
- Magnetostriction oscillator and
- Piezoelectric oscillator.
1.2.1. Galton whistle

Galton whistle works on the principle of organ pipe. It consists of a closed end air column A whose length can be adjusted with the help of a movable piston. The piston P can be moved to the desired position with the help of a screw S1. The open end of the pipe A is fitted with a lip L. The position of the pipe C can be adjusted with the help of the screw S2. The gap between the ends of A and C can be adjusted with the help of the screw S2 (Fig 1.2). An air blast is blown through the nozzle N at the top. The blast of air coming out of C strikes against the lip L and the column of air in the pipe are set in to vibration. By adjusting the length of the air column in A, it is brought to the resonant position. The resonant frequency will depend on the length and diameter of the pipe A. If ‘l’ is the length of the air column in A, x is the end correction, then the wavelength

\[ \lambda = 4(l+x) \]

The frequency of sound is,

\[ n = \frac{V}{\lambda} \]

\[ n = \frac{V}{4(l+x)} \quad \text{where } V = \text{velocity} \]

With the help of this whistle, frequencies of the order of 30,000 Hz can be produced. The micrometer screw S1 can also be calibrated to give directly the frequency of the sound.

1.2.2. Magnetostriction oscillator

Ultrasonic waves can be produced by the principle of magnetostriction. According to this principle, if a ferromagnetic material in the form of a bar is subjected to an alternating magnetic field, the bar expands and contracts alternately. The frequency of contraction or expansion is twice the frequency of the alternating magnetic field.
Fig 1.2  Galton whistle
The alternating magnetic field is produced with the help of an oscillatory circuit. Due to the longitudinal contraction and expansion of the bar, longitudinal compressional waves are produced in the medium surrounding the bar. Frequencies ranging from a few hundred hertz to about 30,000 Hz can be produced with this arrangement. The frequency of the ultrasonic waves produced by this method will depend on the length, density and elasticity of the material of the bar.

1.2.3. Piezo-electric oscillator

This is the most widely used method in the generation of ultrasonic waves. In this method, if a pair of opposite faces of a Piezo-electric crystal is subjected to pressure, the other pair of opposite faces develops opposite electric charges. The sign of the charge changes when the faces are subjected to tension instead of pressure. Curie brothers in 1880 found that certain crystals like quartz, tourmaline and Rochelle salt will develop electric charge, when mechanical pressure or tension is applied to the face of the crystal. Their experiments showed that there is a certain relation between the mechanical pressure applied and the nature of charge developed, and the sign of the charge changed when the pressure was changed to tension. This phenomenon was manifested in many crystals but is very distinctly marked in quartz and Rochelle salt. Quartz crystals have been widely used for generating ultrasonic vibrations in solids and liquids, since they possess high mechanical impedance. Professor Langevein was the pioneer worker in utilizing quartz crystal for ultrasonic work during the first world war, at the same time A.M. Nikolson utilised Rochelle salt for generation of ultrasonics.

1.3. DETECTION OF ULTRASONIC WAVES

Ultrasonic waves propagated through a medium can be detected in a number of ways. Some of the methods employed are as follows:
1.3.1. Kundt’s tube method

Ultrasonic waves can be detected with the help of Kundt’s tube. At the nodes, Lycopodium powder collects in the form of heaps. The average distance between two adjacent heaps is equal to half the wavelength. This method can not be used if the wavelength of ultrasonic waves is very small. In the case of a liquid medium, instead of lycopodium powder, powdered coke is used to detect the position of nodes.

1.3.2. Sensitive flame method

A narrow sensitive flame is moved along the medium. At the position of the antinode, the flame is steady. At the position of the node the flame flickers because there is change in pressure. In this way positions of nodes and antinodes can be found in a medium. The average distance between two adjacent nodes is equal to half the wavelength. If the value of the frequency of the ultrasonic wave is known, the velocity of the ultrasonic wave through the medium can be calculated.

1.3.3. Thermal detectors

This is the most commonly used method of detection of ultrasonic waves. In this method, a fine platinum wire is used. This wire is moved through the medium. At the position of nodes, due to alternate compressions and rarefactions, adiabatic changes in temperature takes place. The resistance of the platinum wire changes with respect to time. This can be detected with the help of Callendar and Griffith’s bridge arrangement. At the position of the antinodes, the temperature remains constant and the resistance of the platinum wire remains constant. This will be indicated by the undisturbed balanced position of the bridge.
1.3.4. Quartz crystal receiver

Just as quartz or Rochelle salt crystals can be used for the generation of ultrasonic waves, they can be also used as detectors of ultrasonic waves. When ultrasonic waves are incident on quartz or a Rochelle salt crystal, alternating electromotive force of the same frequency as the ultrasonic wave is generated. This voltage is very small in magnitude and a radio frequency amplifier can be used to amplify the received signal, which may be detected by a superheterodyne receiver and displayed on the screen of an oscilloscope. This is the universal method for the detection of ultrasonics.

1.4. REVIEW OF THEORETICAL ULTRASONIC STUDIES

Ultrasonic velocity is an important and essential physical parameter having structural dependence. Kneser\textsuperscript{4} proposed the first theory of ultrasonic absorption in liquids. Depending on excess absorption phenomenon Pinkerton\textsuperscript{5} gave a useful classification in liquids. Several theories were proposed to study the ultrasonic velocities in binary and ternary liquid mixtures. They are Jacobson\textsuperscript{6} free length theory, Schaff’s\textsuperscript{7} collision factor theory, Junjie’s expression\textsuperscript{8}, Nomoto’s relation\textsuperscript{9}, Flory’s theory\textsuperscript{10, 11}, Narasimhan and Manikam’s combined equation\textsuperscript{12}, Vandeal ideal mixing relation\textsuperscript{13}, Patterson theory\textsuperscript{14} and Flory-Patterson theory\textsuperscript{10, 11, 14} have been recently used\textsuperscript{15} to obtain the ultrasonic velocity in quaternary liquid mixtures. These theories have been tested\textsuperscript{16}. Based on the additivity of internal energies, the sound velocity in a liquid mixture was determined by Kudriavstev\textsuperscript{17, 18}.

Assuming the linearity of the molecular sound velocity and additivity of molar volume, Nomoto\textsuperscript{9} was able to give an empirical relation for ultrasonic velocity in binary liquid mixtures, which is to be extended successful for quaternary liquid mixtures\textsuperscript{16}.
Expressions of sound velocities of Jacobson, Van Dael's, Schaaffs can be extended to the liquid quaternary system.

Measurement of ultrasonic velocity in liquids and liquid mixtures give information about physico-chemical behaviour of solutions and liquid mixtures such as molecular association and dissociation. It is also used in understanding the molecular interactions in pure liquids. The nature of acoustical and thermodynamic parameters like adiabatic compressibility ($\beta$), intermolecular free length ($L_i$), absorption coefficient ($\alpha/p^2$), free volume ($V_f$), available volume ($V_a$), internal pressure ($\pi_i$), viscous relaxation time ($\tau$), cohesive energy (CE), Rao constant (R) and molecular interaction parameter with respect to velocity ($\chi_v$), density ($\chi_d$) and viscosity ($\chi_n$) which are evaluated by using ultrasonic velocity, density and the viscosity of liquid and liquid mixture provide useful information about the nature of interactions and found to yield information regarding the intermolecular process and the structure of liquids.

1.5. REVIEW OF EXPERIMENTAL ULTRASONIC STUDIES

In the recent past, several researchers have given importance to investigate the molecular interactions through the measurement of ultrasonic velocity, density and viscosity to study the behaviour of solutions and its mixtures. A brief review on application of ultrasonics in the study of pure liquids, binary liquid mixtures ternary / electron donor-acceptor systems and soaps and detergents are presented below.

1.5.1. Pure liquids

According to Erying et al molecules in a liquid state are so loosely packed as to leave some free space in-between them. This free space and its dependent properties are related to the molecular structure and may show some interesting features about the
interaction, which may occur when two or more organic liquids are mixed. A sound wave is regarded as travelling with gas kinetic velocity through space and with infinite velocity through rest of the path. A good deal of work has been reported\textsuperscript{21-26} on the sound velocity and adiabatic compressibility in pure liquids and binary liquid-liquid mixtures.

Chennarayappa et al\textsuperscript{27} have analysed in terms of the structure-breaking and structure-making effects of the components and the influence of alcohol chain length. Isentropic compressibilities have extensive applications in characterising aspects of the physico-chemical behaviour of liquid mixtures, such as molecular association, dissociation and complex formation. Isentropic compressibility data have been determined at 303.15 K for mixture of N-methyl cyclohexylamine with n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, n-pentanol and isopentanol which are self-associated through hydrogen bonding\textsuperscript{28-31}.

Benzene has a well-known planar structure and has a high polarisability. On account of the high polarisability it is possible that induction forces come in to play between benzene and acetic acid increasing the cohesive energy between benzene and acetic acid and decreasing the cohesive energy between acid molecules. Seshariri et al\textsuperscript{32} studied the interaction of carboxylic acids with benzene, carbon tetrachloride and chloroform confirmed the association in carboxylic acids.

1.5.2 Binary liquid systems

The ultrasonic technique for determining several thermodynamic parameters and their bearing on the characteristics of solutions has been used by many workers\textsuperscript{33-38}. Lagemann and Dunbar\textsuperscript{39} established the utility of sound velocity for the qualitative determination of degree of association in liquids. Srivastava et al\textsuperscript{40} reported the acoustical parameters of organometallic compounds in solvents of lower dielectric constant. In the
recent years n-alkoxy ethanol commercially known as cellosolves have drawn the attention of many investigators\textsuperscript{41-45}, to study solute – solvent interactions. Nandi et al have reported conductance and viscosity measurements of a number of alkali metal halides in 2-methoxyethanol\textsuperscript{46,47}.

Binary liquid systems containing organonitrogen compounds like aniline, pyridine, aliphatic amines, alcohols and phenols are characterised by the specific interaction of hydrogen bond formation between unlike components, causing negative deviations from ideal behaviour. Kumar et al\textsuperscript{48} showed that the strength of interaction decreases as the chain length increases in triethylamine and lower aliphatic alcohols from methanol to propanol. Srivastava et al studied with the higher alcohols n-hexanol, n-heptanol and n-dodecanol with a view of seeing the effect of chain length on the strength of interaction with triethylamine\textsuperscript{49}.

It was found that the strength of interaction increases with increase in chain length. The same result was also observed in the system triethylamine + n-octanol and triethylamine + n-decanol\textsuperscript{50}. The decrease in interaction from methanol to n-propanol was explained as increase of alkyl chain decreasing the strength of the hydrogen bonding\textsuperscript{51}. It was observed that the hydrogen bond energies decrease with increasing chain length. But the anomalous behaviour of higher alcohols cannot be explained by this fact. But it is necessary to take geometrical factors in to consideration\textsuperscript{52}. The higher homologues tend increasingly to form cyclic associates as the molecular weight increases.

Ram Lakhan Mishra\textsuperscript{53} have done the theoretical evaluation of velocities for different binary mixtures and derived the molecular interaction parameters. Ultrasonic studies in binary mixtures, considered in terms of excess functions have been of considerable interest during last few decades\textsuperscript{54-59}. Depending upon the nature of liquids, whether they are polar, non-polar or associating, the signs and magnitudes of excess values can throw light on the strength of interactions.
1.5.3 Ternary liquid mixtures / Donor and acceptor systems

Ultrasonic velocity in liquids has been an experimental tool for gaining insight to the nature of the liquid state. Literature shows that various acoustical and thermodynamic parameters have been extensively used to study the molecular interactions in a ternary liquid mixture\textsuperscript{60-63}. The isentropic compressibility and its deviations in different mixtures has been compared with Redlich-Kister theoretical equation\textsuperscript{64} and found satisfactory results\textsuperscript{65-68}.

Arul and Palaniappan\textsuperscript{69} have conducted molecular interaction studies in the ternary mixture of cyclohexane, toluene and 2-propanol. The results have been analysed and observed that there is a formation of cyclohexane-toluene complexes, which are broken by 2-propanol. So the presence of weak interactions are noticed in the ternary system. Presence of electrolyte and non-electrolyte produces different types of interaction in the molecule of solute and the solvent. The effect of addition of an electrolyte with mixed solvents was studied by several authors\textsuperscript{70-73}. Mishra et al\textsuperscript{74} have studied the formation of charge transfer complexes of benzyl chloride and bromobenzene with o-cresol in an inert non-polar solvent using dielectric technique. The complex has been interpreted in terms of dipole moment, interaction dielectric constant and interaction molar polarisation. The extensive search of the literature shows few reports on the ternary / donor-acceptor systems when compared to binary systems.

1.5.4. Soaps and detergents

Ultrasonic measurements provide interesting information on the specificity of the ion-solvent interaction related to the structure of solute and on the reciprocal effects which arise in the solvents. However, ultrasonic studies on soaps and detergents have not drawn adequate attention to give more information on the soap-solvent interaction\textsuperscript{75}. 
A number of workers\textsuperscript{76-79} used ultrasonic measurements for the determination of ion-solvent interaction and the results were found to be in good agreement with those computed by other techniques like NMR\textsuperscript{80}, IR\textsuperscript{81,82} and Raman\textsuperscript{83} studies.

Mehrotra et al studied different types of soaps like Yttrium soap\textsuperscript{84}, Didymium soap\textsuperscript{85}, Lanthanum soap\textsuperscript{86}, Terbium soap\textsuperscript{87} and Thorium soap\textsuperscript{88} solutions. They evaluated the Critical Micelle Concentration (CMC) of soaps and the types of interactions present in these soap solutions.

1.6. PRESENT WORK

The study of propagation of ultrasonic waves in liquids and liquid mixtures is well established for examining the nature of inter-molecular and intra-molecular interactions. Ultrasonic velocity measurements in liquids and liquid mixtures have been an experimental tool for gaining insight into the nature of the liquid state and to understand the physicochemical properties of the components and it can be coupled with the other experimental data such as density and viscosity to calculate various acoustical, thermodynamic and excess thermodynamic functions.

In the present investigation, ultrasonic velocities, densities and viscosities have been measured in binary and ternary mixtures at different temperatures and concentrations to understand different types of molecular interactions and to determine the formation constants of certain donor-acceptor complexes. The compounds chosen are such that the interaction range from very weak induced dipole-induced dipole to strong hydrogen bond.
Critical Micellar Concentration (CMC) and aggregation numbers of three surfactants namely, Sodium Lauryl Sulphate (SDS), Cetyl N,N,N-trimethyl ammonium bromide (CTAB) and TritonX-100 are determined in aqueous medium by ultrasonic and fluorimetric methods. The influence of lipase on the detergent action of three surfactants has been investigated by determining the critical micellar concentration values for three detergents in the presence of lipase at constant temperature and the pH. The removal of dye stain by these surfactants and its enhancement by lipase are investigated.

Kraft temperature has been determined for the above three surfactants with four enzymes namely, lipase, protease, amylase and formaldehyde dehydrogenase. The influence of magnesium sulphate and calcium chloride on the Kraft temperature was studied.
REFERENCES


7. Schauf, W., Acoustica., 30, 1974, 275, 33, 1975, 272


15. Pandey, J.D., Pant, N., Agrawal, N. and Shikha., Acustica., 68, 1969, 225


36. Prakash S. and Prakash, O., Acustica, 32, 1975, 279
50. Prakash, O. and Darbari, S., Acoustics letters., 12, 1988, 35
62. Meiczink, P. and Boch, W., Acustica., 62, 1986, 144
63. Sivakumar, K. and Naidu, P.R., Acoustics letters., 17(5), 1993
70. Piotr Miecznik and Dariusz Madej., Acustica. acta acustica., 85, 1999, 809
73. Piotr Miecznik., Acoustics letters., 2(11), 1988, 213
75. Mahendran, S., Ph.D. Thesis, Madras University, 2002
84. Mehrotra, K.N. and Kirti Tandon., Acoustics letters., 13(11), 1990, 205


86. Mehrotra, K.N., Gahlaut, A.S. and Meera Sharma., Acoustics letters., 1, 3(9), 1990, 163
