CHAPTER – II

Experimental Techniques and Theory of some Acoustical Parameters

Abstract
The experimental methods in measuring the density, viscosity and ultrasonic velocity both liquids and solids (glasses) are presented in detail. In addition, the elementary theories involved in the computation of various acoustical, thermodynamical and transport parameters from experimental data are briefly given.
2.1. INTRODUCTION

This chapter presents the experimental techniques used to measure the ultrasonic velocity, density and viscosity of liquid and liquid mixtures are given in detail. The basic theories involved in calculating the acoustical parameters have also been outlined. The correctness of any experimental measurements is limited not only by the accuracy of the instrument used, but also to a considerable extent, by the purity of the substances used. Impurities change the behaviour of the liquids and mixtures considerably.

All the chemicals used in this present research work are analytical (AR) reagent grade and spectroscopic (SR) reagent grade of minimum assay of 99.9% obtained from E-Merck Germany and Sd Fine chemicals India. The purities of the chemicals were checked by density determination which showed an accuracy of $\pm 1 \times 10^{-4}$ Kg/m$^3$ with the reported values of Dean Lanques (1979) and David (1992). Fresh conductivity water was used throughout the investigation.

2.2 Temperature control

An electronically operated constant temperature bath (RAAGA Industries Chennai) has been used to circulate water through the double walled measuring cell made up of steel
containing the experimental solution at the desired temperature. The bath consisted of an immersion heater, a circulation pump and a digital thermal sensor with display coupled with jumbo type relay to control the variations in temperature. The samples were allowed to stand for 30 minutes in thermostatic water bath to maintain a thermal equilibrium within the bath liquid so that temperature becomes a constant. The accuracy in the temperature measurement is ± 0.1K.

2.3 Measurement of density

Density is one of the prime parameters characterising many physical properties of a liquid medium. Various methods are used for measuring the density of a solution. They are divided into four main categories:

a) Pyknometer / Specific gravity bottle method
b) Magnetic float method
c) Buoyancy method and
d) Balancing column method

The density of pure liquids and liquid mixtures are determined using a specific gravity bottle by relative measurement method. A specific gravity bottle with 5ml capacity is cleaned well and dried and filled with reference liquid (conductivity water) and then suspended in a
temperature controlled water bath. The temperature of the bath can be maintained at any desired value. The bottle with water is allowed to attain the temperature at which density is to be measured and the weight is determined as $W_w$ with an accuracy of $\pm 0.0001\text{gm}$ (Model: SHIMADZU AX-200 Japan). After standardising the specific gravity bottle with water, the liquid whose density to be determined is filled in the bottle and is weighed as $W_s$. By using the following relation, the density of the unknown mixture at any temperature can be determined.

$$\rho_s = \frac{W_s}{W_w} \times \rho_w \quad \ldots \ (2.1)$$

The density of water ($\rho_w$) at different temperatures are taken from literature (John and Dean 1987).
2.4 Measurement of viscosity

The resistance, which one layer of a liquid flowing with one velocity offer to another layer of the liquid flowing with a different velocity is known as viscosity. It depends on the nature of the liquid, temperature and external pressure in addition the shear rate also plays a definite role. The viscosity of the solutions may be measured in number of standard forms of viscometer method. These are

i. Capillary viscometers
ii. Concentric cylinder viscometer (or) Rotation viscometer
iii. Orifice viscometer and
iv. Stoke’s method

The method commonly employed is the capillary viscometer method which is, based on Poiseuilles law. The three types of capillary viscometer are

a. Ostwald’s viscometer
b. Cannon-Fenske viscometer and
c. Ubbelohde viscometer

In the present study, an Ostwald’s viscometer which is 10ml capacity is used for the viscosity measurement of pure liquids, liquid mixtures. The viscometer is calibrated with fresh conductivity water immersed in the water bath which is kept at
the experimental temperature. The efflux time of flow ($t_w$) of water and the time flow ($t_s$) of solution is measured with digital chronometer to within $\pm 0.01$ s (Model: RACER). By knowing the flow time of reference liquid (water) and liquid mixture, the viscosity of the mixture can be determined using the relation

$$\eta_s = \eta_w \frac{\rho_s t_s}{\rho_w t_w} \quad \ldots (2.2)$$

where $\eta_s$, $\rho_S$ and $t_s$ are the viscosity, density and time of flow of solution respectively. $\eta_w$, $\rho_w$ and $t_w$ are the corresponding
quantities for water. The measured viscosity values are accurate to $\pm 3 \times 10^{-6}$ Nsm$^{-2}$.

2.5 Ultrasonic velocity measurement

Longitudinal waves with frequency above 20 KHz are termed as ultrasonic waves. The propagation of an ultrasonic wave in liquids and liquid mixtures is carried out by different methods. An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity, $(U)$ in liquids with degree of accuracy. In ultrasonic interferometer, a piezoelectric crystal slab (like quartz) with parallel faces develops charges of opposite polarity on their faces when it is strained; such a crystal slab exhibits electrostriction when placed in a region of electric field. The speeds of sound in pure liquids and their binary or ternary mixtures were measured using single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, Model:F-81) operating at 2 MHz. The uncertainty in speed of sound measurements was within the range of $\pm 0.1$ms$^{-1}$.

Three techniques are generally used for the measurement of ultrasonic velocity. These are:

1) Pulse Echo technique

2) Optical diffraction technique, and

3) Interferometric technique
Fig. 2.1 Experimental arrangement for the measurement of ultrasonic velocity in liquids.

1. Specific gravity bottle  
2. Ultrasonic Interferometer  
3. Measuring Cell Unit  
4. Viscometer  
5. Constant temperature water bath  
6. Electronic Digital Balance
The speeds of sound using ultrasonic interferometer were studied in detail and further extensive analysis was made to develop the method of high frequency interferometer.

**Description of the interferometer**

The ultrasonic interferometer set up has basically a Wheatstone’s network. Two arms of the network are the load resistance of two identical pentode oscillators, the plate resistances of the pentodes forming the other two arms. The oscillations have been stabilized to a fixed desired frequency by using a quartz crystal oscillator. A micro ammeter is connected between the junctions of the load resistance and the radio frequency choke. This acts as the detector. The output of one of the oscillators is fed to a quartz crystal (of fixed frequency in MHz range) mounted at the bottom of the measuring cell. The cell could be filled up with any liquid whose velocity of sound is to be determined. A reflector can be moved up or down using a screw head. The metal reflector can be kept as close to the crystal transducer as possible. A finite current may be made to pass through the micro ammeter by adjusting the ‘adjust’ and ‘gain’ knobs on the interferometer. The reflector, when moved, can go to such a height so that a standing wave pattern can be formed between the transducer crystal and the reflector. At this
moment the vibrating crystal will draw energy and thus load the oscillator to which it is connected. The loading causes a greater imbalance in the bridge leading to a decrease of current through the micro ammeter. The meter, thus, gives a minimum reading. As the reflector is moved further, the standing wave pattern could not be formed and the meter needle goes back to its original position. The distance ‘d’ moved by the reflector to register two consecutive minimum readings in the micro ammeter corresponds to \( \lambda/2 \) of the ultrasonic wave in the liquid. Thus, a measurement of ‘d’ at a fixed frequency ‘f’ of the oscillator enables one to determine the velocity ‘u’ of propagation of the ultrasonic waves in the given liquid medium. A thermostatically regulated water bath is connected to it to maintain the temperature of the liquid constant during the experiment.

The ultrasonic interferometer is composed of the following parts:

(A) The high frequency generator

(B) The measuring cell
(A) High Frequency Generator

The measuring cell was connected to the output terminal of the high frequency generator through a shielded cable. The cell was filled with approximately 10 ml of test liquid sample before switching on the generator. The vibrations of quartz crystal generate ultrasonic waves in MHz range in the liquid sample, waves move normal from quartz crystal to a movable metallic reflector plate maintained parallel to the crystal surface which reflects these waves and the standing or stationary waves are formed in the liquid between the quartz crystal and the reflector plate. The reflector plate was slowly moved in a downward direction using a micrometer till the anode current on the ammeter of the high frequency generator showed the maximum value. Accordingly, the current on the ammeter went through a number of maxima and minima as the reflector plate was moved downward inside the cell by micrometer. The number of maxima n was counted. To obtain accurate values of \( u \), care should be taken to move the reflector plate only in one direction, preferably, in the downward and at least 15 to 21 maxima values should be recorded to get the value of \( \lambda \).
(B) The measuring cell

It is a specially designed double-walled cell for maintaining a constant temperature of the experimental liquid. A fine micrometer screw is provided at the top of the cell which can lower or raise the reflector plate in the cell containing the liquid through a known distance. It has a quartz crystal fixed at its bottom and connected with the high frequency generator through a shielded cable. Studies on temperature variation on ultrasonic are possible by circulating water at the desired temperature from thermostatic water bath in the measuring cell (Fig.2.2).
Fig. 2.2 Cross-section of the Liquid Cell
Operation of the interferometer

The following precautions are to be taken for the experimental measurements of ultrasonic speed: First find the least count of the screw head attached to the reflector.

a. Fill the cell with the experimental liquid so that the cell is 3/4\textsuperscript{th} full. Fix the reflector unit on top of the cell. Mount the cell in the given sturdy base. Connect the output cable from the ultrasonic apparatus to the socket provided on the metal base.

b. Switch on the ultrasonic apparatus. Keep the ADJUST and GAIN knobs in the minimum position. After a minute the meter reading will register a maximum. Wait for some more time (i.e. additional minute). The meter will come back to zero reading on the dial.

c. Turn the GAIN knob to a maximum. The reading in the meter may be around 50 or 60 microamperes. Now, turn the knob so that the meter reading is around 80 microampere.

d. Turn the screw gauge head such that the pitch scale reading is at the least. In this position, the reflector is closer to the crystal – the source of ultrasonic vibrations. Let the screw be turned and the reflector moved up. The
meter reading in the ultrasonic interferometer will change. Note the head scale as well as the pitch scale reading when the micro ammeter reading is the least.

**Calculation of Speed of Sound**

Measurement of ultrasonic velocity using ultrasonic interferometer is based on determining the wavelength \((\lambda)\) of ultrasonic wave in the medium. The plate current is maximum corresponding to the variation of the reflector distance by half wavelength or integral multiple of half wavelength. The ultrasonic velocity is calculated by the following relation:

\[
\lambda = \frac{2d}{n}
\]

where \(d\) is the total distance moved by the micrometer screw for a maximum or minimum deflection, \(n\) is the number of maxima or minima of anode current for a distance \(d\). The following relation gives the ultrasonic velocity through a liquid

\[
U = \lambda \cdot f
\]

Thus, on substituting the value of \(d\) and \(f\) is the frequency of the quartz crystal (2 MHz) used we get the value of ultrasonic velocity. The accuracy of ultrasonic velocity measurement is \(\pm 0.5\%\).
Precautions to be taken

1. The generator should always be switched on after filling the experimental liquid in the cell.

2. After the experimental liquid was taken out, the cell should be kept clean and dry.

3. The micrometer should be kept open at 25 mm after use.

4. Sudden rise or fall in temperature of the circulated liquid should be avoided to prevent thermal shock to the quartz crystal.

5. While cleaning the cell, care must be taken not to spoil or scratch the gold plating on the quartz crystal.

6. Usually 15 minutes should be given for warming up the generator (interferometer).

2.6 Pulse Echo Technique (Glasses)

A high energy pulse-receiver (Panametrics5058 PR) used to measure ultrasonic velocity in glasses is shown in Fig.2.4. The measurement of ultrasonic velocity depends upon generating a dynamic pressure wave into a material of known thickness and measuring the transit time of emerging acoustic pressure wave. A piezoelectric transducer usually accomplishes this generation and detection of an acoustic wave. These transducers are more adoptable to extreme range of frequency, have greater conversion efficiency and provide the greatest sensitivity and hence are more frequently used than the magnetostrictive transducers.
Generally, the equipment selected for ultrasonic testing of solid materials typically fall into one of the categories, based on the following measured parameters.

1. Amplitude of reflected energy only

2. Amplitude and transit time of reflected energy and

3. Loading of the transducer by the test object.
Fundamentals

While the ultrasonic testing methods like the through-transmission method use the amplitude information alone, the pulse-echo method, the most versatile technique for ultrasonic testing of solid materials, uses two parameters simultaneously that are

The amplitude of the signals obtained from internal discontinuities (and/or boundary of the specimen) and time required for the beam to travel between specific surfaces and these discontinuities (or specimen boundary). The block

Fig. 2.3 Experimental arrangement for the measurement of ultrasonic velocity in glasses. Inlet: Transducer with sample
diagram of pulse-echo testing system, also called as the A-scan equipment is shown in Fig. 2.4.

A short electric pulse is applied to the electrodes of the transducer. This produces a short train of elastic waves that are coupled to the test object. Timing circuits then measure the interval between the transmitted pulse and the reception of signals from the test objects. This cycle is repeated at regular periods, (at the rates varying from 60Hz to 10 KHz). The pulse repetition rate on the pulse-echo system is adjusted so that reverberations within the test object decay completely between the pulses and the vertical deflection shows signal amplitudes. As mentioned earlier the horizontal sweep is proportional to the time, so that the transit times of the pulse to and from the reflector and to and from the back wall respectively corresponds to the distance on the screen from the initial peak to echo peaks corresponding to reflector and back wall. To obtained a standing image, the pulses and sweep of the Cathode Ray tube are synchronized is called pulse-repetition frequency. By calibration of the baseline in time per unit length, the transit time‘t’ to the reflector and the back wall respectively can be read from the screen.
Fig. 2.4 Block diagram of pulse echo testing system

Fig. 2.5 Cross-section of buffered ultrasonic transducer for materials characterization using pulse echo method
Since the distance ‘d’ travelled is twice the thickness of the specimen, the velocity of sound can be calculated as

\[ U = \frac{2d}{t} \quad \ldots \quad (2.4) \]

2.7. Sample Preparation for glass.

The chemicals used in the present research work were Analytical Reagent (AR) and Spectroscopic Reagent (SR) grade with minimum assay 99%. The chemicals weighed in mole percentage (mol%) by increasing the mole percentage of \( \text{B}_2\text{O}_3 \), doped with \( \text{PbO} \) and \( \text{P}_2\text{O}_5 \) which both lie on decreasing scale of mole percentage. The required amounts (approximately 20g) in mol% of chemicals in powder form were weighed using single pan digital balance (Model SHIMADZU AX 200-Japan make) having an accuracy of 0.0001g. The homogenization of the appropriate mixture of the component of chemicals was effected by repeating grinding using a pestle and mortar. The temperature in the temperature controlled muffle furnace was gradually raised to a higher temperature at the rate of 100K per hour and a glassily structure was noticed for BML glass system at 1060K and for BSP glass system 1080K and eventually the molten glass melt was
immediately poured on a heavy copper moulding block having the dimensions of 12mm diameter and 6 mm length kept at room temperature. The glass samples were then annealed at 400K for two hours to avoid the mechanical strains developed during the quenching process.
2.8 Theory and calculations

2.8.1. Adiabatic compressibility ($\beta$)

The electrostatic field produced by the interacting atoms in the solution influences the structural arrangement of the molecules, which in turn has pronounced effect on compressibility. When acoustical wave passes through a medium, adiabatic compression and rarefaction takes place. This results in a change in pressure ($\delta P$) and a corresponding change in volume ($\delta V$).

Hence, the adiabatic compressibility 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 the thermodynamic relation [Rowbinson and Swinton (1982)].

$$\beta = \frac{1}{V} \left( \frac{\delta V}{\delta P} \right) \quad \ldots(2.5)$$

It can also be calculated from the speed of sound ($U$) and the density of the medium ($\rho$) using the equation of Newton and Laplace as

$$\beta = \frac{1}{U^2 \rho} \quad \ldots(2.6)$$
2.8.2. Intermolecular free length ($L_f$)

In the liquid state of matter, molecules are loosely packed, leaving free space among them. Propagation of sound waves through this space is regarded to be that of gas kinetic velocity and infinite velocity through the rest of this path. The intermolecular free length $L_f$ in liquids are generally defined as

$$L_f = \frac{2V_a}{Y} \quad \text{...(2.7)}$$

where $V_a$ is the available volume and $Y$ the total surface area per mole and the same is given as

$$Y = \left(36\pi N V_0^2 \right) \quad \text{...(2.8)}$$

Here $V_0$ is the molar volume at 0 K. The available volume is related to molar volume as

$$V_a = V_T - V_0 \quad \text{...(2.9)}$$

where $V_T$ is the molar volume at T(K)

$$\text{Thermodynamically, } V_0 = V_T \left(1 - \frac{T}{T_C}\right)^{0.3} \quad \text{...(2.10)}$$

where $T_C$ is the critical temperature,

$$\text{Hence } L_f = \frac{2(V_T - V_0)}{(36\pi N V_0^2)^{\frac{1}{3}}} \quad \text{...(2.11)}$$

It was shown by Schaaffs (1975) that
\[ V_0 = S \cdot B \quad \text{... (2.12)} \]

where \( S \) and \( B \) are collision factor and geometrical volume respectively. Hence,

\[ V_a = V_T - S \cdot B \quad \text{... (2.13)} \]

Schaaffs also expressed the ultrasonic velocity \( U \) in terms of \( SB \).

\[ U = U_\infty \left( \frac{SB}{V} \right) \quad \text{... (2.14)} \]

where \( U_\infty \) is the limiting velocity and is taken as 1600 ms\(^{-1}\). Hence combining (2.12) and (2.14).

\[ V_a = V_T \left( 1 - \frac{U}{U_a} \right) \quad \text{... (2.15)} \]

Determination of intermolecular free length in liquids and in liquid mixtures has been a subject of considerable interest. Jacobson (1952) established a semi-empirical relation to achieve the concept of intermolecular free length in order to explain the ultrasonic velocity in liquids.

\[ L_I = K_T \sqrt{B} \quad \text{... (2.16)} \]

where \( K_T \) is a temperature dependent constant. Its values are
Table 2.1: The values of $K_T$ at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>303</th>
<th>308</th>
<th>313</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_T$ values in SI system</td>
<td>$199.53 \times 10^{-8}$</td>
<td>$201.1209 \times 10^{-8}$</td>
<td>$203.0182 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

The intermolecular free length depends on the type of packing and extent of association in a given liquid. This provides the strongest evidence of the applicability and utility of the equation (2.16) for liquid systems.

2.8.3. Free volume ($V_f$)

Free volume is one of the significant factors in explaining the variations in the physico-chemical properties of liquids and liquid mixtures. 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. This molecular interactions between like and dislike molecules are influenced by structural arrangements along with shape and size of the molecules. A liquid may be treated as if it were composed of individual molecules each moving in a volume $V_f$ in an average potential due to its neighbours. That is, the molecules of a liquid are not quite closely packed and there are some free spaces between the molecules for movement and this volume is called the free volume $V_f$ (Glasstone, 1950). Thirumaran and
Indhu, 2009 free volume as the effective volume in which particular molecule of the liquid can move and obey perfect gas laws. Glasstone et al., (1941) have related the free volume per molecule as

\[ V_f = V \left( \frac{bRT}{\Delta E_{vap}} \right)^3 \]  

...(2.17)

where \( b \) is the packing factor of the molecule and \( \Delta E_{vap} \) is the energy of vaporisation per mole of the liquid. Ramamoorthy and Alwan (1978) computed free volume from calculated \( \Delta E_{vap} \) using an empirical formula, which on comparison with standard values proved to be poor in accuracy.

Eyring and Kincaid proposed another method which related free volume of liquid in terms of ultrasonic velocity in liquid, the sound velocity in vapour \( U_g \) and the molar volume (V) as

\[ V_f = \left( \frac{V}{U_g^3} \right) \left( \frac{\gamma RT}{M} \right)^{3/2} \]  

...(2.18)

where \( \gamma \) is the ratio of the two specific heat capacities \( (\gamma = C_p/C_v) \), \( R \), the universal gas constant, \( T \), the temperature and \( M \), the molecular weight respectively.

Based on the dimensional analysis, Suryanarayana and Kuppusamy (1976) obtained a relation for free volume in terms of ultrasonic velocity (U) and the viscosity of the liquid (\( \eta \)) as
\[ V_f = \left( \frac{M_{\text{eff}} U}{K \eta} \right)^{3/2} \] ... (2.19)

where \( M_{\text{eff}} \) is the effective molecular weight \( (M_{\text{eff}} = \sum m_i x_i) \), in which \( m_i \) and \( x_i \) are the molecular weight and the mole fraction of the individual constituents respectively. \( K \) is a temperature independent constant which is equal to \( 4.28 \times 10^9 \) for all liquids.

The advantage of this equation is that it no longer requires the constants like expansivity \( (\alpha) \), specific heat at constant pressure \( (C_p) \) and vapour pressure or energy of vaporisation \( (\Delta E_{\text{vap}}) \) of the medium to obtain free volume. The relation has a direct bearing on molecular size of the aggregate of the self associated species through the term containing the viscosity, which is a physical description of the relaxation phenomenon. On comparing equations (2.18) and (2.19), the former equation requires \( \gamma \) and \( \gamma \) is not a routinely measured property and it requires precision equipment to measure \( C_p \). On the other hand in equation (2.19), \( \eta \) is routinely measured parameter and sensitive property of a liquid. Hence, Suryanarayana (1989) preferred equation (2.19) over equation (2.18) for the estimation of \( V_f \).

2.8.4. Internal pressure \( (\pi_i) \)

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal
pressure is a cohesive force, which are the resultant attractive and repulsive forces between the molecules (VanderWaal’s, 1873; Richards, 1925; Hildebrand and Scott 1950). Cohesion creates a pressure within the liquid in between $10^3$ and $10^4$ atmospheres. However, when external pressure exceeds 5000 atmosphere, internal pressure begins to decrease rapidly and becomes large negative values as the liquid is further compressed showing that the repulsive forces become predominant. This pressure may be regarded as a measure of the pressure in the interior of the liquid. The attractive forces mainly comprised hydrogen bonding, dipole-dipole, multipolar and dispersion interactions. Repulsive forces, acting over a very small intermolecular distances, play a minor role in the cohesion process under normal circumstances. Dipolar liquids have higher internal pressure than normal liquids (Dack, 1975; Glasstone, 1947).

Internal pressure also gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, coulombic or Vander Waal’s interactions. The term $a/v^2$ in Vander Waal’s equation being the measure of attractive force of the molecule is called the cohesive or internal pressure.

The internal pressure is the single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent
interactions. A general method of measuring the internal pressure (Hildebrand and Scott, 1950) based on the Maxwell’s equation of thermodynamics

\[ P = T \left( \frac{\partial P}{\partial T} \right)_V - \left( \frac{\partial E}{\partial V} \right)_T \]  

...(2.20)

The first term in the right hand side is the product of temperature and temperature co-efficient of pressure and second term is the internal pressure. The equation may be rewritten as

\[ \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \]  

...(2.21)

The thermal pressure \( P \) is negligible compared to the value of \( T \left( \frac{\partial P}{\partial T} \right)_V \), which is thousands of atmosphere. Hence, the equation reduces to

\[ \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - \left( \frac{T_\alpha}{\beta_T} \right) \]  

...(2.22)

where \( \alpha \) is the coefficient of cubical expansion and \( \beta_T \) is the isothermal compressibility. Hence by measuring these quantities one can determine the internal pressure of the system. The above method is susceptible for criticism since the temperature coefficient of pressure has relevance to the case of
an ideal gas whereas for condensed systems (liquids) it gives misleading results.

Suryanarayana (1960) has considered all these factors and derived an expression based on the relation between surface tension and intermolecular forces as suggested by Young (1905) and also incorporating the observations made by Hildebrand and Scott (1962),

\[ \pi_i = \left( \frac{C_1}{C_2} \right) \left( \frac{\rho^4}{M} \right)^{1/3} \]  

\( \ldots(2.23) \)

where \( c_1 \) and \( c_2 \) are constants. The computable part of the equation i.e., \( \left( \frac{\rho^4}{M} \right)^{1/3} \) was called \( \pi_i \) factor. Because of complexities involved in evaluating the non-computable part of the equation i.e. \( \frac{C_1}{C_2} \), Suryanarayana (1979) derived a qualitative relation between surface tension and internal pressure in liquid system as

\[ \pi_i = \left( \frac{bRT}{C^{1/6}} \right) \left( \frac{\gamma^{1/6}}{M^{2/3} V_f^{1/3}} \right) \]  

\( \ldots(2.24) \)
where $b$ is the cubic packing which is assumed to be 2 for all liquids and solutions and $C$, the concentration in gram moles/litre.

On the basis of statistical thermodynamics, Suryanarayana (1979) derived an expression for the determination of internal pressure by the use of free volume concept as

$$V_f = \frac{1}{V^2} \left( \frac{bRT}{P + \left( \frac{\partial E}{\partial V} \right)_T} \right)^3 \quad \text{...(2.25)}$$

As $\left( \frac{\partial E}{\partial V} \right)_T$ is the internal pressure and neglecting $P$ which is insignificantly small to $\pi_i$, the equation can be written as

$$V_f = \frac{1}{V^2} \left( \frac{bRT}{\pi_i} \right)^3 \quad \text{...(2.26)}$$

The final equation for the evaluation of internal pressure can be obtained by combining and rearranging the equation (2.25) and (2.26) as

$$\pi_i = bRT \left( \frac{K\eta}{U} \right)^{1/2} \left( \frac{\rho^{2/3}}{M_{eff}^{7/6}} \right) \quad \text{...(2.27)}$$
This equation has been tested for a number of liquids and solution of electrolytes Kannappan and Rajendran (1992) and non-electrolytes Suryanarayana (1989).

2.8.5. Viscous relaxation time ($\tau$)

Viscous relaxation time describes the rate at which molecules return to their original positions after being displaced by force. The dispersion of the ultrasonic velocity (Herzfeld and Litovitz, 1959) should contain information about the characteristic time of the relaxation process that causes absorption. The relaxation time is estimated from the following relation (Bender and Pecora, 1986):

$$\tau = \frac{4}{3} \eta \beta$$  \hspace{1cm} ... (2.28)

Knowing the viscosity of the liquid ($\eta$) and the adiabatic compressibility ($\beta$), $\tau$ can be calculated.

2.8.6. Gibb’s Free Energy ($\Delta G^*$)

The relaxation time for a given transition is related to activation free energy. The variation of $\tau$ with temperature (Bender and Pecora, 1986) can be expressed in the form of Eyring rate process theory:

$$\frac{1}{\tau} = \frac{KT}{h} \exp \left[ \frac{-\Delta G^*}{KT} \right]$$
The above equation can be rearranged:

$$\Delta G^* = -2.303 \, KT \, \log \frac{h}{KT\tau} \quad \ldots \quad (2.29)$$

where $K$ is Boltzmann’s constant and $h$ is the Planck’s constant.

### 2.8.7. Excess Values ($A^E$)

In order to study the non-ideality of the liquid mixtures, the difference between the parameters of the real mixture ($A_{exp}$) and those corresponding to an ideal mixture ($A_{id}$) values, namely excess parameters ($A^E$) of all the acoustic parameters were computed by the relation

$$A^E = A_{exp} - A_{id} \quad \ldots \quad (2.30)$$

where $A_{id} = \sum_{i=1}^{n} A_i \, X_i$, $A_i$ is any acoustical parameters and $X_i$ the mole fraction of the liquid component.

### 2.8.8. Gunberg’s Interaction Parameter (d)

Viscosity data for ternary mixtures have yielded information regarding the nature of the interaction (Salas et al., 2006, Surabhi and Mukhtar 2002). For the viscosity of such ternary mixtures, we have used in equation (2.31) suggested by Grunberg and Nissan (1949)
\[
\ln \eta_{\text{mix}} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_3 \ln \eta_3 + X_1 X_2 X_3 \quad \text{...(2.31)}
\]

where \( \eta_{\text{mix}} \) is the viscosity of mixtures \( \eta_1, \eta_2 \) and \( \eta_3 \) are the viscosity of pure liquids. \( X_1, X_2 \) and \( X_3 \) are the mole fractions of the component of the mixtures. ‘d’ is proportional to \( W/RT \) and \( W \) is the interchange energy. The parameter has the same significance as given by Guggenheim (1952) in the treatment of regular solution theory and ‘d’ has regarded as better measure of the strength of molecular interactions between the components in solution.

2.8.9. Molar Hydration Number (\( n_H \))

In solutions, the electric force originating from an ion becomes zero only at infinity. However, the force fades out to a negligible value after quite a short distance. Beyond this cut off distance, solvent molecules may be regarded as unaware of an ion’s presence. There is therefore a certain effective volume around the ion within which its influence operates. The number of solvent molecules that are available in this volume could be participating in the solvation of the ion. This number may be termed as Molar hydration number.

Though innumerable number of techniques both theoretical and experimental is available for obtaining solvation,
compressibility method (Jasmine Vasantharani, 1997) is found to yield accurate information.

The compressibility $\beta$ is defined by the expression

$$\beta = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T$$

... (2.32)

If a pure solvent is considered, then its compressibility may be written as

$$\beta = -\left(\frac{1}{V}\right)\left(\frac{dV}{dP}\right)_T$$

... (2.33)

In an ionic solution, the solvent has been treated as an open framework structure with many gaps in it. When pressure is applied, the solvent molecules enter into the interstitial space and the solvent molecules become more tightly packed than earlier and hence volume gets decreased.

Another way of compressing the solvent is by introducing ions into the solvent, as they are capable of wrenching solvent molecules out of the solvent framework so as to envelop themselves with solvent sheaths. Because the molecules are oriented in the ionic field, the solvent is more compactly packed in the primary solvation shell as compared to the packing if the ions were not there. The solvent has become compressed by the
introduction of the ion. The origin of the influence of the ion is the electric field of the ion. Thus, electric field causes compression of the material medium upon which they exert their influence, this phenomenon is known as electrostriction.

Since the introduction of ions makes the primary solvent shell to be highly compressed and these solvent molecules may be supposed to respond to any further pressure which may be applied. Thus, the compressibility of an ionic solution is less than that of the pure solvent because of the incompressibility of the primary solvation sheath. Outside the primary solvent sheath, the solvent molecules are not oriented to the same degree as those inside the primary solvation sheath because the orienting ionic field is less. This means that the non-primary solvation shell has the same compressibility as the pure solvent.

The ratio of compressibility of a solvent ($\beta_0$) to that of the solution ($\beta$) can be calculated by the following way. Suppose the primary molar hydration number is $n_{\text{H}}$, then $n_2$ moles of solute are solvated with $n_2 n_{\text{H}}$ moles of incompressible solvent. Now if $n_1$ $n_2$ moles of solvent correspond to a total volume $V$ of solution, $n_2 n_{\text{H}}$ moles of incompressible solvent should correspond to a volume $V n_{\text{H}} n_2/n_1$ of incompressible solution. Defining the symbol $Y$ as
\[ Y = \frac{n_1 n_2}{n_1} \quad \ldots (2.34) \]

The volume of the incompressible part of the solution is \( Y_V \). This volume must be excluded from the expression from the compressibility of the ionic solution.

Thus, \[ \beta = -\left( \frac{1}{V} \right) \left( \frac{\partial (V - Y_V)}{\partial P} \right)_T \]

\[ \beta_0 = -\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial P} \right)_T \]

\[ \frac{\beta}{\beta_0} = 1 - Y \]

Hence from equation (2.34)

\[ \frac{\beta}{\beta_0} = 1 - \left( \frac{n_1 n_2}{n_1} \right)_T \]

\[ n_1 = \left( \frac{n_1}{n_2} \right) \left( 1 - \frac{\beta}{\beta_0} \right) \quad \ldots (2.35) \]

This equation is used to obtain the molar hydration number by determining the compressibility of aqueous solution.

2.8.10. **Apparent molar compressibility** \( (\varphi_k) \)

When an electrolyte is dissolved in a solvent, it decomposes partly or completely into ions. In solutions the molar volumes of solute and solvent differ from their molar volumes in pure form. This change in volume and hence change in pressure
leads to partial molar compressibility for the solvent and solute. Thus, the apparent molar compressibility of the solute is the compressibility of an amount of solution of one mole of solute minus the compressibility of the solvent and is given by the relation,

$$\varphi K = \frac{1000}{m\varphi_0} (\rho_0 \beta - \rho \beta_0) + \left( \frac{\beta_0 M}{\rho_0} \right)$$

...(2.36)

where, $\beta$, $\rho$ and $\beta_0$, $\rho_0$ are the adiabatic compressibility and density of solution and solvent respectively, $m$ is the molar concentration of the solute and $M$ the molecular mass of the solute. $\varphi K$ is the function of ‘$m$’ as obtained by Guckar (1933) from Debye Huckel theory (Thirumaran and Job sabu 2009) and is given by

$$\varphi K = \varphi K^0 + S_K m^{\frac{1}{2}}$$

...(2.37)

where $\varphi K^0$ is the limiting apparent molar compressibility at infinite dilution and $S_K$ is a constant. $\varphi K^0$ and $S_K$ were obtained by least square method.

2.8.11. Apparent molar volume ($\varphi_v$)

The apparent molar volume $\varphi_v$ of the solute is the volume of the amount of solution containing one mole of the solute minus the volume of solvent present in the solution.
The apparent molar volume of a solute is related to the density, molar compressibility etc. of the solution. The volume change may be due to

i) the contraction of volume as the dissolved salt may absorb solvent and

ii) the ability of the solute to cause electrostriction (Jerry March 1984, Volkenshtein 1983). The apparent molar volume may be obtained as

$$\varphi_{V} = \frac{1000}{m\rho_{0}}(\rho_{0} - \rho) + \left(\frac{M}{\rho_{0}}\right)$$ ... (2.38)

The apparent molar volume has been found to differ with concentration according to Masson’s empirical relation (Masson 1929) as

$$\varphi_{V} = \varphi_{V}^{0} + S_{V}m^{1/2}$$ ... (2.39)

where $\varphi_{V}^{0}$ is the limiting apparent molar volume at infinite solution and $S_{V}$ is a constant and these values were determined by least square method.

2.8.12. Partial Transfer Volume ($\Delta\varphi_{V}^{0}$)

Transfer volumes of each amino acids, $\Delta\varphi_{V}^{0}$ from water to aqueous solutions have been calculated by the equation

$$\Delta\varphi_{V}^{0} = \varphi_{V}^{0} \text{ (in aqueous solution)} - \varphi_{V}^{0} \text{ (in water)}$$ ... (2.40)
where $\Delta \varphi^0_v$ denotes transfer volume.

2.8.13. Viscosity B-coefficient

Among the various parameters to study solute-solvent interaction, the easily measurable viscosity and density are preferred. Viscosity studies of amino acids in mixed solvent systems is one of the most fundamental transport properties that play a vital role in understanding the solution behaviour of the amino acids. The importance of viscometric study of electrolyte solution in mixed solvent systems is well established (Chauhan et. al., 2002; Patial et. al., 2002). The entire viscosity data have been analysed in the light of Jones-Dole semi empirical equation (Jones and Dole 1929).

$$\frac{\eta}{\eta_0} = 1 + Am^{\frac{1}{2}} + Bm \quad \ldots (2.41)$$

The same in the form of equation of straight line is

$$\left(\frac{\eta}{\eta_0}\right) - 1 = \frac{A + Bm^{\frac{1}{2}}}{m^{\frac{1}{2}}} \quad \ldots (2.42)$$

where $\eta$ and $\eta_0$ are the viscosities of the solution and solvent respectively and ‘m’ is the molar concentration of the solute-solvent system. A is known as Falkenhagen coefficient (Thirumaran and Job Sabu, 2009) which characterises the ionic interaction and B is the Jones-Dole or viscosity B-
coefficient which depends on the size of the solute and nature of solute-solvent interactions.


The ultrasonic longitudinal and shear velocities of the prepared glass specimen were determined by using the pulse-echo method at room temperature at 5 MHz using X-cut and Y-cut transducers. These transducers act as both transmitters and receivers of the ultrasonic pulse. The transducers were brought into contact with each of the twelve samples by means of a couplant, in order to ensure that there was no air void between the transducer and the specimen. By applying constant pressure on the probe the echo waveforms were obtained on the display unit and stored in the memory. Figures 2.6 and 2.7 show one such echo waveforms obtained for longitudinal and shear waves.
Longitudinal and shear waves

Fig. 2.6. Longitudinal wave form

Fig. 2.7. Shear wave form
2.8.15. Measurement of Density

The density of the glass samples was measured using relative measurement method. Benzene was used as a buoyant liquid. The glass samples were weighed both in air and after immersing in benzene at 303K. The weight of the glass samples was measured in a single pan with an accuracy of 0.0001 g. The density was calculated using the formula

$$\rho = \rho_B \frac{W_1}{W_1 - W_2}$$

where, $W_1$ and $W_2$ are the weights of the glass samples in air and in benzene and $\rho_B$ is the density of the benzene at 303K.

2.9. Parameters Evaluated

The elastic and mechanical properties of the glass specimen were calculated at room temperature by using the measured values of density ($\rho$), longitudinal velocity ($U_l$) and shear velocity ($U_s$).

2.9.1. Longitudinal modulus (L)

The ratio between longitudinally applied stress and the longitudinal strain (Bhattia et al., 1973, Mason 1965) is obtained for longitudinal wave propagation as

$$L = \rho U_l^2 \quad \ldots \text{2.43}$$
2.9.2. Shear modulus (G)

The shear modulus can be found from shear velocity, which is found in materials that sustain shearing forces (mostly solids and viscous fluids) as

\[ G = \rho U_s^2 \]  

... 2.45

2.9.3. Bulk modulus (K)

The ratio between bulk stress and bulk strain is obtained from the ultrasonic velocities as

\[ K = L - \frac{4}{3}G \]  

... 2.46

2.9.4. Poisson’s ratio (\( \sigma \))

It is axiomatic that the elastic constant are all interrelated. Therefore, once the isotropic moduli are established, poisson’s ratio (\( \sigma \)) may be calculated, as this also a function of the ratio of the longitudinal and shear velocities. It is gives by the relation

\[ \sigma = \left( \frac{L - 2G}{L \cdot G} \right) \]  

... 2.47

2.9.5. Young’s modulus (E)

This is defined as the ratio between unidirectional stress and the resultant strain and is given in terms of the ultrasonic velocities \( U_l \) and \( U_s \) as
\[ E = (1 + \sigma) 2G \quad \ldots \quad 2.48 \]

2.9.6. Acoustic impedance (Z)

The transmission and reflection of sound energy in the glass specimens was determined using the acoustical impedance

\[ Z = U_1 \rho \quad \ldots \quad 2.49 \]

2.9.7. Microhardness (H_v)

Microhardness is given by

\[ H_v = \left( \frac{(1 - 2\sigma)E}{6(1 + \sigma)} \right) \quad \ldots \quad 2.50 \]

Where E and \( \sigma \) have the usual meanings

2.9.8. Debye temperature (\( \theta_B \))

The Debye temperature (\( \theta_B \)) of the sample is calculated from the relation

\[ \theta_B = \left( \frac{h}{K_B} \left( \frac{9N}{4\pi V_m} \right)^{1/3} U_m \right) \quad \ldots \quad 2.51 \]

where, h, \( K_B \), N, \( V_m \), and \( U_m \) are the plank’s constant (6.626 \times 10^{-34} \text{JS}), the Boltzmann’s constant (1.38 \times 10^{-23} \text{JK}^{-1}), the Avagadro’s number (6.023 \times 10^{23} \text{mol}^{-1}), the molar volume and mean sound velocity of the sample respectively
\[ U_m = \left[ \frac{1}{3} \left( \frac{2}{U_i^3} + \frac{1}{U_l^3} \right) \right]^{\frac{1}{3}} \]

2.9.9. Thermal expansion coefficient (\( \alpha_p \))

Thermal expansion coefficient can be obtained (Padakis et al., 1976) as

\[ \alpha_p = 23.2 (U_i - 0.57457) \quad \ldots \, 2.52 \]