Chapter Two

The properties of liquids

2.1 Prologue

Liquid state is the most abundant form present on earth. Physical properties of liquids are very important because they are characteristic of each liquid. Sound velocity, density, refractive index etc are some of the physical properties which are characteristic of each liquid. The properties of liquids can be broadly classified into bulk thermodynamic and mechanical properties, static optical and electrical properties as well as the relevant molecular properties (size, shape, charge, polarizability, dipole moment etc). These properties depend on the condition under which the liquid is studied viz., temperature and pressure. Wherever possible, liquids will be reviewed at comparable reduced temperatures and pressures i.e., at corresponding states. In the previous chapter we have discussed about the different types of liquids, intermolecular interactions and intermolecular forces in them. A brief description of liquid mixtures and solutions is also made. In the present chapter an attempt has been made to explain the important properties of liquids viz., density, ultrasonic velocity, refractive index, surface tension, viscosity, adiabatic
compressibility and specific acoustic impedance. Some of the earlier works in the field of ultrasonic velocity, adiabatic compressibility and specific acoustic impedance are also discussed. A large number of ultrasonic, thermodynamic and optical studies were conducted to probe the physico-chemical behaviour of liquids and liquid mixtures. All these studies have made significant advances in the fundamental knowledge of liquid properties and in understanding the physical structure of liquid state [33].

2.2 Thermodynamic properties of phase transitions in liquids

Small changes in energy $E$, enthalpy $H$, the Helmholtz free energy $A$, and the Gibbs free energy $G$ and entropy $S$ are given by the four fundamental equations for systems of constant composition and total mass.

\[
\begin{align*}
\frac{dE}{dT} &= T \frac{dS}{dT} - P \frac{dV}{dT} \\
\frac{dH}{dT} &= T \frac{dS}{dT} + V \frac{dP}{dT} \\
\frac{dA}{dT} &= -S \frac{dT}{dT} - P \frac{dV}{dT} \\
\frac{dG}{dT} &= -S \frac{dT}{dT} + V \frac{dP}{dT}
\end{align*}
\]

It follows that

\[
\begin{align*}
\left( \frac{\partial E}{\partial V} \right)_S &= \left( \frac{\partial A}{\partial V} \right)_T = -P \\
\left( \frac{\partial H}{\partial P} \right)_S &= \left( \frac{\partial G}{\partial P} \right)_T = V \\
\left( \frac{\partial A}{\partial T} \right)_V &= \left( \frac{\partial G}{\partial T} \right)_P = -S
\end{align*}
\]

The first order transitions are characterized by definite differences between the molar properties of the liquid and solid or gas.
\[ \Delta y^F = y' - y^s \]  
(2.8)
is the difference on freezing between the generalized property \( y \) of liquid and solid, and similarly,
\[ \Delta y^V = y^g - y' \]  
(2.9)
for evaporation. The superscripts \( F \) and \( V \) denote freezing and evaporation. The quantities \( \Delta y^F \) and \( \Delta y^V \) are normally positive. These property changes of freezing and evaporation are functions of temperature and of pressure. The changes are moderate, and over a short range of \((T, P)\) the functions \( \Delta y^F \) and \( \Delta y^V \) can be considered as constants [5, 6].

2.3 Density of liquids

The density \( \rho \) of a liquid is its mass per unit volume or the reciprocal of its specific volume. If \( n_0 \) is the number of molecules per unit volume and \( m_0 \) the mass of each molecule, then density

\[ \rho = m_0 n_o \]  
(2.10)

If \( M \) is the molecular weight of the liquid and \( N \) the Avagadro number, then

\[ m_0 = \frac{M}{N} \]  
(2.11)

Therefore

\[ \rho = \frac{n_0 M}{N} \]  
(2.12)

Generally when temperature increases, the density decreases. Under normal pressures, a liquid has a density which is not too dissimilar from that of the solid. This is true over the whole liquid range from the melting point to the boiling point. At the melting point, generally liquid is less dense than solid. But there are a few exceptions, of which water is one, ice floats on water.
Silicon, germanium and tin are other examples where the liquid is more dense than the solid. This is because solids have rather open crystal structures with the low coordination number of four. This statement is not applicable to liquids near their critical points which are much less dense. For example, water has density of only $0.32 \times 10^3 \text{ kgm}^{-3}$ at its critical point so that it expands in volume by about a factor of three on going from its normal melting point to the critical point. A liquid close to its critical point has more free space between the molecules than does the normal liquid [34].

2.4 Molar volume and density

Molar volume of a liquid is the volume occupied by one mole of the liquid. The relation between the molar volume and chemical composition of liquids was studied by Kopp who finally adopted the boiling point as the standard temperature of comparison. The results obtained by Kopp are

(i) A constant difference in composition corresponds with a constant difference in molar volume.

(ii) Isomeric substances of similar constitution have the same molar volume.

(iii) The influence of one carbon atom is the same as that of two hydrogen atoms.

(iv) Replacement of hydrogen by an equivalent of oxygen makes only a slight change in molar volume.

From Eq. (2.12)

$$\frac{M}{\rho} = \frac{N}{n_o}$$

(2.13)

is the molar volume of the liquid. The density and the molar volume of a liquid depend on the magnitudes of state, the pressure and the temperature [35, 36].
2.5 Variation of density with temperature

The influence of temperature on the density of a liquid is very considerable, and is not the same for the various organic compounds. It is true that the coefficient of thermal expansion of numerous organic liquids do not differ greatly from one another. The average value of coefficient of thermal expansion of organic liquids is about one part per thousand of the density per degree Kelvin.

\[ \frac{1}{\rho} \left( \frac{dp}{dT} \right) \approx -10^{-3} \]  \hspace{1cm} (2.14)

where \( T \) is in Kelvin.

Since the densities of many organic substances lie between 700 and 1200 kgm\(^{-3}\), the different volume changes lie within a ratio of 1:2 [36].

2.6 Index of refraction of liquids

Another property which is commonly used in the study of liquids is its index of refraction. It is defined as the ratio of the sine of the angle of incidence of a ray of light in air or vacuum to the sine of the angle of refraction in the medium. It is also equal to the ratio of the velocity of light in air or vacuum to the velocity of light in a medium. The ray of light undergoes changes in wave velocity and in direction at the boundary interface and these changes are dependent on temperature \( T \) and wavelength \( \lambda \) of light. The refractivity formula proposed by Beer, Gladstone and Dale is

\[ \frac{(n-1)}{\rho} = r_G \]  \hspace{1cm} (2.15)
and by Lorenz and Lorentz is

$$\frac{(n^2 - 1)}{(n^2 + 2) \rho} = r_L$$  \hspace{1cm} (2.16)

where \( n \) is the refractive index and \( \rho \) is the density of the liquid and \( r_G \) and \( r_L \) are constants.

Multiplying Eq. (2.15) and (2.16) by \( M \), the molecular weight of the liquid, we get molecular refractivity or molar refractivity

$$R_G = M r_G = \frac{(n - 1) M}{\rho}$$  \hspace{1cm} (2.17)

and

$$R_L = M r_L = \frac{(n^2 - 1) \left( \frac{M}{n^2 + 2} \right)}{\rho}$$  \hspace{1cm} (2.18)

These are also constants for a particular liquid if \( n \) is determined for a wavelength \( \lambda \) [37, 38].

Empirical relations connecting refractive index and density of liquids were derived by Mohanan et. al. [39, 40]. They found that

$$\frac{n}{\rho^{0.45}} = \nu$$  \hspace{1cm} (2.19)

where \( \nu \) is a constant called specific optical volume. Molar optical volume \( N \) of a liquid was obtained by multiplying \( \nu \) by the molecular weight \( M \) of the liquid and is given by

$$N = \frac{M n}{\rho^{0.45}}$$  \hspace{1cm} (2.20)
It is also a constant for a given liquid. It can be decomposed into elemental values. It exhibits constitutive and additive properties similar to molar refraction \( R_L \) [39].

Again the specific optic impedance \( Z_o \) is defined as

\[
Z_o = \frac{120 \pi \rho}{n}
\]  (2.21)

where \( \rho \) is the density and \( n \) is the refractive index of a liquid [40].

### 2.7 Variation of index of refraction with temperature

For a given wavelength, the index of refraction decreases with increase in temperature. This decrease is not the same for all liquids. It varies slightly from compound to compound. The change in index of refraction from compound to compound is related to changes in structure. Usually the temperature at which refractive index is determined is specified to be 293 or 298 K. The former is more in accord with past practice, but the latter is somewhat easier to maintain with a constant temperature bath under ordinary laboratory conditions. The wavelength usually specified is that of the yellow sodium \( D \) line [41, 42].

### 2.8 Surface tension of liquids

It is the fundamental property of liquid surfaces which is related to internal forces in a liquid. The existence of surface tension suggests that the surface of a liquid may be regarded as a stretched membrane enclosing the bulk of the liquid. The boundary layer between a liquid phase and a gas phase may be considered as a third phase with properties intermediate between those of a liquid and a gas. A qualitative picture of the microscopic surface layer shows
that there are unequal forces acting upon the molecules. Thus the surface layer is in tension and tends to contract to the smallest area. Surface tension $\sigma$ of a liquid is the force acting tangential to the liquid surface per unit length tending to decrease the surface area. The strength of surface tension is directly related to the strength of intermolecular attractions. A liquid with high intermolecular attractions will have higher surface tension than a liquid with weak attractions. As the temperature is raised, the surface tension of a liquid in equilibrium with its own vapour decreases and becomes zero at the critical point. Surface tension is very sensitive to the density of liquids chosen [43, 44].

2.9 Effect of temperature on surface tension

According to kinetic theory, molecular kinetic energy is proportional to absolute temperature. The rise in temperature of a liquid therefore is accompanied by increase in energy of its molecules. The intermolecular forces of attraction, therefore decrease with rise in temperature. Hence surface tension of a liquid decreases with rise in temperature. At critical temperature, since the surface of separation between a liquid and its vapour disappears, the surface tension falls to zero. Eotvos found that surface tension varies linearly with temperature. He suggested the variation of surface tension with temperature as

$$\sigma \left( \frac{M}{\rho} \right)^{2/3} = a - kT$$

(2.22)

where $M$ is the molecular weight, $\rho$ is the density and $\sigma$ is the surface tension of the liquid at temperature $T$ and $a$ and $k$ are constants.

At critical temperature (i.e., when $T = T_c$), the surface tension is zero.
Eotvos equation may be rewritten as

\[ \sigma \left( \frac{M}{\rho} \right)^{2/3} = k (T_c - T) \]  \hspace{1cm} (2.23)

This equation has been found to be satisfactory for a number of liquids over a wide range of temperature [35, 45].

2.10 Viscosity of liquids

Liquids, like gases, exhibit the resistance to its flow which is known as viscosity. In general it is the property which opposes the relative motion of adjacent layers of the liquid and so it may be regarded as an internal friction. The ability of a liquid to flow in response to external forces is a characteristic property which implies that the molecules are able to rearrange themselves, rather than being fixed in definite unchanging order as in a perfect crystal. Viscosity depends on molecular size and particularly length and also on the magnitude of the intermolecular forces. Non-polar organic liquids (e.g., benzene) generally have low viscosities whereas liquids in which directed bonding can occur between the molecules (e.g., hydrogen bonds in glycerol) have relatively high viscosities [46].

2.11 Effect of pressure and temperature on viscosity of liquids

Rontgen showed experimentally that for all liquids except water, the viscosity increases with increase in pressure. The viscosity of water decreases as pressure increases. Ladenburg found that viscosity \( \eta \) for viscous mixtures of resin and turpentine was practically doubled under 100 atm pressure. The viscosities of liquids invariably decrease markedly with rise of temperature (roughly about 2% per degree) and follows fairly closely the Andrade equation namely,
\[ \eta v^{1/3} = A e^{c/vT} \]  \hfill (2.24)

in which \( A \) and \( c \) are constants for a given liquid and \( v \) is the specific volume.

Batschinski proposed an interesting empirical relationship which appears to be closely obeyed by a number of non-associated liquids over a wide range of temperature. The relation is

\[ \eta = \frac{c}{v - w} \]  \hfill (2.25)

where \( v \) is the specific volume of the liquid measured at the same temperature as the viscosity, \( c \) and \( w \) are constants for each liquid \([46, 47]\).

### 2.12 Viscosity of mixtures

The equation proposed by Bingham to represent the mixtures of two liquids is

\[ \phi = x_A \phi_A + x_B \phi_B \]  \hfill (2.26)

where \( \phi \) is the fluidity of the mixture which is the reciprocal of coefficient of viscosity and \( \phi_A \) and \( \phi_B \) are the values for the two pure components whose molefractions in the mixture are \( x_A \) and \( x_B \) respectively. Mixtures of similar liquids (e.g., benzene and toluene) behave ideally. If constituents of the mixture form complexes in the liquid state (e.g., mixture of amine and phenol), the observed fluidities are less than the calculated values and then there is a considerable increase of viscosity upon mixing. Water and ethanol mixtures exhibit this type of behaviour, probably as a result of hydrogen bond formation between water and alcohol molecules. Mixtures of two dissimilar liquids (e.g., a polar and a non-polar liquid such as alcohol and benzene) usually have higher fluidities and lower viscosities. Such mixtures exhibit positive deviations from ideal behaviour \([8, 47]\).
2.13 Ultrasonic sound velocity in organic liquids

The studies of sound velocity, its temperature and pressure dependence and attempts to relate the sound velocity to the physical structure of the liquid have led to the development of an extensive literature in this field. The first extensive measurements of ultrasonic velocity in organic liquids were carried out by Parthasarathy. He pointed out that aromatic compounds, usually have higher velocities than the corresponding aliphatic compounds, although their densities are higher. Velocity in liquids of high density is low, but not in proportion, the increase in density being to some extent set off by an accompanying decrease in compressibility. Polar molecules favour high velocities, long molecules give rise to higher velocities, a double bond of unsaturation tends to lower velocity and in similar derivatives, change from a light to a heavy atom lowers velocity. The velocity of ultrasonic waves in liquids (except water) decreases with increasing temperature. For water, the velocity of ultrasound propagation increases with increasing temperature until it reaches a maximum at 347K and then decreases [48, 49].

Schaaffs [50] has derived an expression for Van der Waal’s constant ‘b’ in terms of ultrasonic velocity \( U \), molecular weight \( M \), density \( \rho \) and absolute temperature \( T \).

\[
b = \frac{M}{\rho} \left[ 1 - \frac{RT}{MU^2} \left( \sqrt{1 + \frac{MU^2}{3RT}} - 1 \right) \right] \tag{2.27}
\]

It has been shown that ‘b’ is an additive function, and its value for atoms can be computed. These values can then be used to compute the value of ‘b’ for any other compound. Schaaffs pointed out that ‘b’ is four times the molecular volume. For spherical molecules ‘b’ is related to molecular volume by
where $r$ is the molecular radius and $N$ is the Avagadro number [49, 51, 52].

2.14 Rao’s molar sound velocity

There have been many attempts to calculate the ultrasonic velocity in a liquid from molecular parameters. In a wide range of liquids, associated and non-associated and including molten salts, the ultrasonic velocity decreases linearly with increasing temperature over a considerable range of temperature. Deviations from this linear relation occur near the boiling point and melting point of liquids. Rao observed that the approximately linear dependences of sound velocity $U$ and molar volume $V$ of liquids were related by the expression

$$
\frac{1}{U} \left( \frac{\partial U}{\partial T} \right)_p \approx -3 \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p
$$

where $\frac{1}{U} \left( \frac{\partial U}{\partial T} \right)_p$ is the temperature coefficient of sound velocity and $\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ is the temperature coefficient of molar volume respectively.

Integrating Eq. (2.29) we get

$$
U^{1/3} V = R
$$

where $V$ is the molar volume and $R$ is a constant for a given liquid. This constant is known as molar sound velocity or Rao number or Rao’s constant for a liquid which is independent of temperature and contains additive contributions from the various atomic groupings within the liquid molecules. Eq. (2.30) is known as Rao’s formula.
Rao’s formula can also be rewritten as

$$U^{1/3} \left( \frac{M}{\rho} \right) = R$$  \hspace{1cm} (2.31)$$

where \( M \) is the molecular weight and \( \rho \) is the density of the liquid.

Rao also found that the value of \( R \) underwent regular increments among the members of a homologous series of liquids. Such series make it possible to express \( R \) as a linear function of the molecular weight \( M \), as

$$R = a_1 M + a_2$$  \hspace{1cm} (2.32)$$

where \( a_1 \) and \( a_2 \) are constants and the constant \( a_1 \) characterizes the series.

Rao’s rule can also be written as

$$\frac{1}{\beta_s} \left( \frac{\partial \beta_s}{\partial T} \right)_p = 7\alpha$$  \hspace{1cm} (2.33)$$

where \( \alpha \) is the expansion coefficient of a liquid [49, 51, 53].

A parameter called specific opto-acoustic velocity \( \eta \) which is a relation between ultrasonic sound velocity \( U \) in a liquid and the refractive index \( n \) of it was deduced by Mohanan et. al. [39] and is given by

$$\eta = \frac{U^{0.15}}{n}$$  \hspace{1cm} (2.34)$$

It is a constant for a liquid. The molar opto-acoustic velocity was obtained by multiplying \( \eta \) by the molecular weight \( M \) of the liquid and is given by

$$H = \frac{MU^{0.15}}{n}$$  \hspace{1cm} (2.35)$$
$H$ is also a constant for a liquid. Its additive and constitutive properties were studied by them.

2.15 Sound velocity in binary liquid mixtures

The measurement of sound velocity in a vast number of binary liquid mixtures have been done by several workers [54-60]. Calculation of Rao's constant $R$ indicates that the dependence of $R$ is linear in many, but not all cases. In the study of the sound velocity in liquids, Wada suggested that the molecular compressibility $B$ should be a pressure-independent quantity, depending only on the temperature for a pure liquid

$$B = \left( \frac{M}{\rho} \right) \beta_s^{-1/7} \quad (2.36)$$

where $\beta_s$ is the adiabatic compressibility of the liquid.

It has been suggested by Nomoto that $B$ has a linear dependence on the molefraction for all known binary mixtures except those of the water-alcohols, for which the curve is slightly convex upwards. While this result is purely empirical, it does indicate a property that appears to be an additive function of the molecular concentrations of the two species [51, 61].

2.16 Sound velocity and its excess values

Ultrasonic study of thermodynamic parameters in liquid mixtures is of both practical and theoretical importance. The more quantitative idea about the nature of molecular interactions in liquid systems is given by calculating deviation from ideal behaviour and this deviation can be best expressed in terms of excess thermodynamic functions. A departure from linearity in the velocity versus composition behaviour in liquid mixtures is taken as an indication of the existence of interaction between the different species [62, 63].
Nambinarayanan et. al. carried out ultrasonic velocity studies in the solutions of oxalic acid in tetrahydrofuran. They found that the measured ultrasonic velocity increases non-linearly over the entire concentration range studied and the results are discussed on the basis of formation of hydrogen bonds between the oxalic acid and the tetrahydrofuran molecules [64].

The ultrasonic velocity in binary liquid mixtures of N,N - dimethylaniline, cyclohexane and aniline with m-cresol as the common component has been studied by Palaniappan et. al. They made an attempt to calculate the percentage deviation of velocity from Nomoto’s and Van Dael and Vangeel’s ideal mixture relations and the results are explained on the nature and extent of molecular interactions in the mixtures [65].

Nikam et. al. studied ultrasonic velocities in aqueous ethanol solutions of monochloroacetic acid in the concentration range 0.05-0.4 mol / litre at 298 to 313 K at an interval of 5 K. They found that the variation of velocity with temperature is always non-linear. They explained this non-linearity on the basis of solute-solvent interaction in the system [66].

Agnihotri et. al. evaluated ultrasonic velocity in binary liquid mixtures of alcohols + hexane, alcohols + benzene and alcohols + acetone using FLT, CFT and Nomoto relation. The theoretical values are then compared with experimental ones and the results are discussed in terms of self association in alcohols [67].

Prasad and Nath employed ultrasonic velocity measurement technique for the estimation of sugar content in commercially available beverages. Different techniques for sugar content determination have then been compared with ultrasonic velocity measurement technique [68].
Excess sound velocity $U^E$ in binary liquid mixtures 2, 2, 2-trifluoroethanol -1-OH + benzene, benzene + dimethyl sulfoxide and 2, 2, 2-trifluoroethanol -1-OH + dimethyl sulfoxide at 298.15K has been evaluated by Ramanjappa et al. They found that $U^E$ is negative for the first system and positive for the other two systems. The results are then discussed in the light of molecular interactions in these mixtures [69].

Ultrasonic study of 1:1 mixture of ethyl acetate / butyl acetate and phenol / n-butyl alcohol in CC14 (low concentration range) have been carried out at 303 K by Madhu et al. They found that ultrasonic velocity shows a maxima for the two mixtures containing phenol and the third one containing ethyl acetate and n-butyl alcohol. The mixture containing butyl acetate and n-butyl alcohol exhibits an increase of velocity with increasing concentration. They explained the results as an indication of complex formation between unlike molecules through hydrogen bonding [70].

Gokhale and Bhagvat used 'Rao specific sound velocity' to evaluate ultrasonic velocities in binary liquid mixtures of di-n-butylamine with 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol. The same values were also calculated using Nomoto's formula. They found that better agreement between the observed values of the ultrasonic velocities and the calculated ones is achieved when Rao's specific sound velocities along with the density values of binary liquid mixtures were used [71].

Ragouramane and Srinivasa Rao conducted ultrasonic studies in water-rich aqueous solutions of ethylene glycol (EG) in the solute (EG) concentration ranging from 0 to 30% by volume proportions. They found that ultrasonic velocity increase with increase of EG concentration indicating the possibility of complex formation between water and EG molecules. They also studied the
influence of various electrolytes on the ultrasonic velocity in the above aqueous water - EG solution and the results are explained on the structure making and breaking property of the electrolytes in the above solutions [72].

2.17 Compressibility of Liquids

Liquids cannot support a static shear stress. Therefore the only modulus that can be used to define a liquid is its bulk modulus $K$. Liquids are more compressible than solids and much less compressible than gases. The compressibility of a liquid is usually small and numerically comparable with that of a solid. Excepting water, which has a minimum compressibility at about 318K, liquids become more compressible when they are heated. The fractional rate of charge of volume (or density) with pressure at constant temperature is called the isothermal compressibility $\beta_T$. It is otherwise defined as the reciprocal of the isothermal bulk modulus and is written as

$$\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T$$  \hspace{1cm} (2.37)

where $\rho$ is the density of the liquid. On the other hand, if the entropy of the liquid remains constant, adiabatic compressibility $\beta_S$ is obtained as

$$\beta_S = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_S$$  \hspace{1cm} (2.38)

where $S$ is the entropy of the liquid.

Canton was the first to demonstrate experimentally the compressibility of liquids by observing the movement of a liquid in a capillary attached to a bulb filled with the liquid. He found that water and mercury occupied different volumes when they were cooled from a higher temperature to a lower in an
open or in a sealed thermometer. Further he found that the compressibility of water decreases with rise in temperature. Spirit of wine and olive oil were found more compressible than water whereas mercury was found to be less compressible [35, 73].

### 2.18 Compressibility values of liquids

The measurement of compressibilities of liquids using different methods and apparatus gives the following results. They are

(i) the compressibility of a liquid is small, a few hundred-thousands \((10^{-5})\) of the initial volume per atmosphere, that of mercury being very small \(39.6 \text{TPa}^{-1}\) and that of ether relatively large \(1673.3 \text{TPa}^{-1}\).

(ii) the compressibility increases markedly with temperature, two to five times between 273 and 373K. An exception for this is water which shows a minimum value at about 323K.

(iii) the change with temperature is smaller at higher pressures.

(iv) the compressibility decreases as the pressure increases, and the values for different liquids tend to become equal at very high pressures [35, 73].

### 2.19 Compressibility Formulae

The effect of temperature \(T\) on the compressibility of water was represented by Tait by the equation

\[
\frac{AV}{AP} = \frac{A}{(B + P)(C + T)}
\]

(2.39)

where \(A, B\) and \(C\) are constants at a given temperature, \(V\) and \(P\) are the volume and pressure of water. He found that the compressibility decreases with rise of
pressure and temperature and the compressibility of sea water is 0.92 times that of fresh water.

Tumlirz proposed the equation

\[(P+p) (V-b) = \text{constant}\]  \( (2.40) \)

where \( p \) and \( b \) are constants for the expression of a liquid at a given temperature. He found this equation to be in good agreement with experimental value.

Rao found for the effect of temperature on the adiabatic compressibility \( \beta_S \) as

\[ (V^{1/3} / M \beta_S)^{1/2} = k (T_c - T) \]  \( (2.41) \)

where \( V \) is the molar volume, \( M \) is the molecular weight, \( T_c \) is the critical temperature and \( k \) is a constant for each liquid. He found that the adiabatic compressibility is related to density \( \rho \) as [35]

\[ \beta_S^{1/3} \rho = \text{constant} \]  \( (2.42) \)

### 2.20 Adiabatic compressibility and its excess values

Excess parameters can be used to investigate the nature and relative strength of molecular interactions in binary, ternary and multicomponent liquid mixtures. Non ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration. These deviations can be interpreted as due to the presence of strong or weak interactions in the mixtures. The extent of deviation depends on the nature of the constituents and the composition of the mixtures. An important acoustic parameter which is used extensively in the study of liquids and liquid mixtures is adiabatic compressibility \( \beta_S \). It has a direct link with the velocity of sound. It provides
information regarding molecular association, dissociation, hydrogen bonding between components, solute-solvent interaction, complex formation etc and gives a better insight into the intermolecular forces and different types of interaction in a liquid system [74-76].

Rajendra Naidu and Naidu P.R. determined the adiabatic compressibilities of four binary liquid mixtures of n-octane with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol at 303.15K. They found that excess adiabatic compressibility $\beta_s^E$ is positive over the whole composition range for the first two systems and both positive and negative for the remaining two systems. They explained the sign and magnitude of the deviation in the light of changes in intermolecular free space [77].

Ramamurthy et. al. used adiabatic compressibility and intermolecular free-length and their deviations from ideal behaviour for studying the binary mixtures of di-n-butylamine with n-alcohols and explained the results as due to the existence of strong H-bond interaction between unlike molecules [78].

Rajkumar et. al. studied adiabatic compressibilities and viscosities of binary mixtures of isobutanol with n-hexane, n-heptane and cyclohexane and the binary mixtures of 1, 2 - dichloroethane + n-alcohol at 308.15K. They found that adiabatic compressibilities of all these mixtures exhibit positive deviation whereas the viscosities exhibit negative deviation from ideal behaviour. They explained the results as due to breaking up of hydrogen bonds in alcohols by the addition of an alkane or 1, 2-dichloroethane [79].

The adiabatic compressibility, inter molecular free length and molar volume of binary mixtures of allyl alcohol with 1, 4-dioxane and CC1$_4$ and their excess values were studied by Rajaguru and Jeyaraj and the results are
interpreted in terms of hetero-molecular interactions in the allylalcohol + 1, 4 -dioxane system and dispersion forces in the allylalcohol + CC14 system [80].

Ultrasonic studies in binary mixtures of N-methyl cyclohexylamine with alcohols at 303.15K were conducted by Chennarayappa et. al. They found that all the mixtures exhibited negative deviations for adiabatic compressibility which are attributed to hydrogen bond interaction between unlike molecules [81].

Purnachandra Rao reported the excess adiabatic compressibilities of N, N - dimethylformamide and N, N-dimethylacetamide with aliphatic esters at 303.15K. The excess values were positive for certain systems and negative for certain other systems. He explained the result in terms of the effects of carbon chain length and chain branching of esters on the specific interactions between unlike molecules [82].

Excess volumes and deviations in adiabatic compressibilities for the binary mixtures of acetonitrile with alcohols were determined by Dharmaraju et. al. They found that the excess parameters are positive for all the systems and are attributed to weak complex formation and dissociation of associated alcohols by acetonitrile [83].

Seshadri and Subrahmanyam studied excess adiabatic compressibility and excess dielectric constant for the liquid mixtures of morpholine with n-butyl alcohol, iso-butyl alcohol and tertiary-butyl alcohol. The positive and negative values of excess parameters were explained in terms of solute-solvent interaction and steric hindrance of hydrogen bonding in alcohol [84].

Nikam et. al. studied the molecular interactions in binary mixtures of chlorobenzene with normal alkanols using acoustic properties such as adiabatic compressibility \( \beta_S \) and inter molecular free length \( L_f \) at different temperatures. They found that both \( \beta_S \) and \( L_f \) exhibit negative deviation for all systems which
indicates the presence of strong interaction in the system. Moreover they found that with increase of temperature, the excess values of $\beta_s$ and $L_f$ become more negative. They explained this effect as due to thermal dissociation of the homo and hetero aggregates in liquid mixtures and more interstitial accommodation of chlorobenzene molecule into expanded aggregates of alcohols at higher temperature [85].

Padmasree and Ravindra Prasad conducted ultrasonic study of ethylacetate + n-butanol at different temperatures on the basis of excess compressibilities, excess volumes, excess internal pressures etc and the results are explained on the basis of molecular interactions in them [86].

2.21 Impedance

Impedance $Z$ is often described as the ratio of a ‘push’ variable $q_p$ (such as voltage or pressure) to a corresponding ‘flow’ variable $q_f$ (such as current or particle velocity).

$$Z = \frac{q_p(x, y, z, t)}{q_f(x, y, z, t)}$$ (2.43)

The three different impedances which are in common use in acoustics are (a) acoustic impedance (b) specific acoustic impedance and (c) mechanical impedance.

(a) Acoustic impedance

Acoustic impedance at a given surface is the ratio of the sound pressure averaged over that surface $P_{av}$ to the volume velocity $q$ of the fluid through the surface.

$$Z_{ac} = \frac{P_{av}}{q}$$ (2.44)
(b) Specific acoustic impedance

It is the ratio of the pressure at a point \( P \) to the particle velocity \( v \) at the point.

\[
Z_A = \frac{P}{v} \quad (2.45)
\]

(c) Mechanical impedance

It is the ratio of the force \( F \) acting on a specified area to the particle velocity \( v \) through that area.

\[
Z_{mech} = \frac{F}{v} \quad (2.46)
\]

For any wave whose pressure is constant over a specified area \( S \), we have \( P_{av} = P \), \( q = Sv \) and \( F = PS \). In this case Eq. (2.44) and (2.46) reduces to

\[
Z_{ac} = \frac{P}{Sv} = \frac{Z_A}{S} \quad (2.47)
\]

and

\[
Z_{mech} = \frac{PS}{v} = Z_A S \quad (2.48)
\]

Of the three impedances represented by Eq. (2.45), (2.47) and (2.48), the most commonly encountered is the specific acoustic impedance [87].

2.22 Difference between electrical impedance and specific acoustic impedance

Specific acoustic impedance at a point in a field of sound is defined in Eq. (2.45) as

\[
Z_A = \frac{P}{v}
\]

where \( P \) and \( v \) are the instantaneous excess pressure and particle velocity respectively. For a single sound frequency, \( P \) and \( v \) are not necessarily in phase
for all types of waves. Hence specific acoustic impedance, pressure and particle velocity are related exactly as are electrical impedance $Z_E$, potential difference $V$ and current $I$ in an a.c circuit. The most important distinction is that electrical impedance, defined as

$$Z_E = \frac{V}{I}$$

exists between two points in the current carrying circuit whereas the specific acoustic impedance is a point property. Just as the product $VI$ represents instantaneous electrical power, so the product $Pv$ represents the instantaneous acoustical power at the point. However, the power $VI$ is the total power delivered to the circuit across which the potential difference exists, whereas the acoustical power $Pv$, since it involves the pressure, is the energy flow per unit area per unit time [33, 61].

### 2.23 Specific acoustic impedance for plane waves

The plane wave equation is given by

$$\frac{\partial^2 \phi}{\partial t^2} = U^2 \frac{\partial^2 \phi}{\partial x^2}$$

(2.50)

where $U$ is the velocity of sound wave and $\phi$ is the velocity potential. Its solution for a wave travelling in the positive $X$-direction is

$$\phi (x, t) = A \cos \frac{2\pi}{\lambda} (U t - x)$$

(2.51)

In exponential form

$$\phi (x, t) = A e^{ik(Ut - x)}$$

(2.52)
where \[ k = \frac{2\pi}{\lambda} \]

Making use of \[ P = \rho \frac{\partial \phi}{\partial t} \], we find that
\[
P = i \rho k U A e^{ik(Ut-x)} \tag{2.53}
\]

where \( P \) is the instantaneous excess pressure.

Also the particle velocity
\[
v = -\frac{\partial \phi}{\partial x} = i k A e^{ik(Ut-x)} \tag{2.54}
\]

Hence specific acoustic impedance \( Z_A \) is given by
\[
Z_A = \frac{P}{v} = U \rho \tag{2.55}
\]

Thus \( Z_A \) can be defined as the product of velocity of sound in a medium and density of that medium.

In the case of travelling plane waves, pressure and particle velocity are related to each other as follows: [33, 87]

For forward travelling waves \[ P = Z_A v \tag{2.56} \]

For backward travelling waves \[ P = -Z_A v \tag{2.57} \]

### 2.24 Specific acoustic impedance and its excess values

The deviation of the experimental values of specific acoustic impedance from the ideal mixing values for a liquid mixture is referred to as excess
specific acoustic impedance. The excess values may be positive or negative. The sign and magnitude of the values give an insight into the nature of molecular interactions in a liquid mixture. Literature survey shows that only a few attempts have been made in interpreting the molecular interactions in terms of specific acoustic impedance. The mathematical relations for specific acoustic impedance and adiabatic compressibility show that their behaviour is opposite, as $\beta_S = 1 / Z_A U$. The conventional approach based on compressibility is useful and fundamental. However, the impedance approach serves equally well.

Bhavani et al. explained the deviations in specific acoustic impedance $Z_A^E$ from ideal behaviour for the binary mixtures acetonitrile + benzene, benzene + dimethylformamide and acetonitrile + dimethylformamide in terms of solute-solvent interactions [88].

Studies of Subba Rao et al. on 2-ethylbutanol + hexane isomer systems using excess specific acoustic impedance $Z_A^E$ and excess sound velocity $U_E^E$ also throw light into the nature of solute-solvent interactions in these mixtures [89].

Chauhan et al. showed that in the case of acetonitrile (AN) + Propylene carbonate (PC) mixture, the non-linear dependence of acoustic parameters such as specific acoustic impedance, free length, free volume etc and their excess functions as a function of solvent composition and temperature is attributed to the existence of dipolar interactions between the solvent components in AN-PC mixtures [90].

Ultrasonic study of ammonium soaps in 2-propanol had been done by Varma and Surendra Kumar using specific acoustic impedance and other thermodynamic parameters. They explained the increase in the value of $Z_A$ with increase in soap solution on the basis of iyophobic interaction between the
intermolecular distance which leaves a relatively wider gap between the molecules and thus becoming the main cause of impediment to the propagation of ultrasonic waves [91].

Ramanjappa et. al. evaluated $Z^E_A$ and $U^E$ in the binary liquid mixtures of n-heptane with di-n-propylether, 3,6-dioxaoctane and 2,5,8-trioxanonane. They found that both $Z^E_A$ and $U^E$ exhibit positive deviations for the first two systems whereas the third system exhibit positive as well as negative deviation. The results are explained in terms of solute-solvent interaction in the mixtures [92].

The effect of isomeric butanols on the temperature corresponding to specific acoustic impedance maximum of water has been studied by Manohara Murthy et. al. and the results are discussed on the basis of solute-solvent interactions leading to the modification of the hydrogen bonded structure of water by the alcohols [93].