CHAPTER 1
GENERAL REVIEW

1.1 INTRODUCTION:

A number of theoretical relations between ultrasonic velocity, density, freclengt, adiabatic compressibility etc have been established. Relations between acoustic impedance, ultrasonic velocity and density have been conventionally used to study molecular interaction. This gives to the sound velocity, a property of basic importance in molecular theory of liquids. A more important application of sound velocity measurements in liquids has been the evaluation of adiabatic compressibility. There are many records of measurement of ultrasonic velocity, adiabatic compressibility [Padmavatee et al (1995), Venkatesu et al (1996), Kalidoss et al (1997)] and dielectric constant of organic liquids [Prakash et al (1987), Khanna et al (1998)]. Very few attempts seem to have been made to study molecular interaction in polymers using physical properties such as ultrasonic velocity, viscosity, dielectric constant and viscous relaxation time. Extensive use of polymeric material in technology has led, in recent years to increased interest in the various problems of physics and chemistry of polymers.

There are large number of physical properties such as ultrasonic velocity, adiabatic compressibility acoustic impedance, free length, surface tension, free volume, internal pressure, viscosity, relaxation time, dielectric polarisation, electrical conductivity etc, capable of revealing information on molecular interactions. Different techniques have been used to study physical properties, such as microwave absorption measurements [Deogaonkar et al (1982)], refractometric measurements [Sahai et al (1979)], calorimetric measurements [Iordanov et al (1972)] and spectrophotometric measurements [Bhowmik et al (1979)]. Although spectrophotometric method has been extensively used to study molecular complexation, yet as per Sahai et al (1980), this technique is incapable of giving satisfactory results.

As very few attempts seem to have been made to study molecular interaction in polymers we thought it worth attempting. Ultrasonic velocity, viscosity and dielectric
constant measurement techniques being reasonably accurate [Asole (1990)], we have used these in our study.

1.2 PHYSICAL PROPERTIES AND MOLECULAR INTERACTIONS:

Physical properties play an important role in studying molecular interactions. According to Ramamoorthy et al (1973), because of molecular interaction, volume of the mixture changes, which affects the ultrasonic velocity of the mixture. This departure from linearity is attributed to the existence of molecular interaction between the two components of the system. Internal pressure, which is the resultant of forces of attraction and repulsion between molecules, helps in elucidating molecular interactions. Rajasekaran et al (1997) studied the relationship between internal pressure and free volume for rubber solutions. They have concluded that the exponent has a strong dependence on the nature of interactions among the components, and that constant $k$ increases with temperature.

Various acoustical parameters such as isentropic compressibility ($K$), acoustic impedance ($Z$), Rao's molar sound velocity ($R$), internal pressure ($\pi$), intermolecular free length, classical absorption coefficient ($\alpha/l^2$), viscous relaxation time ($\tau$), solvation number ($S_n$) etc. can be calculated by using density, viscosity and ultrasonic velocity. The relative viscosity and viscous relaxation time plots can reveal polymer-polymer chain entanglement. This can help in the interpretation of solvent-polymer and polymer-polymer interactions.

Nucleic acids are the fundamental structural units of compounds of biological relevance. Ultrasonic and volumetric studies of the conformational properties of these molecules, interactions of their different chemical groups with water molecules, the temperature dependence of these interactions etc. have an important role in understanding the thermodynamic behaviour of biochemical processes in living cells. Aswar (1997), while studying molecular interaction in binary mixtures of biomolecules, observed that, the relative change in sound velocity per unit concentration can be a convenient parameter for describing the inter and intra-molecular interactions. Rajulu et al (1995) suggested that adiabatic compressibility may be used for detection of molecular interactions between polymer and solvent. Stieber et al (1987) reported
ultrasonic measurements on polybutadiene-polystyrene copolymer in toluene and explained the results on the basis of polymer-polymer interactions. Kalyansundaram et al (1996) reported interaction between (PMMA) polymer and solvent from the increase in ultrasonic velocity and decrease in the value of adiabatic compressibility with increase in concentration of solute.

Viscosity of a fluid is that characteristic which exhibits certain resistance to alteration of form. Positive deviation of viscosity from ideal behaviour of liquid mixture arises from strong molecular interaction between unlike molecules.

Compatibility of the two polymers can be estimated by the behaviour of their solutions. Also nature of compatibility can be established from nature of the curves of ultrasonic velocity against concentration of a component.

The distribution of charges represents electrical characteristics of a molecule. The investigation on such characteristics gives useful information on many properties. The complex formation is indicated by maximum in dielectric constant [Mulay et al (1987)].

1.3 IMPORTANCE OF POLYMERS:
The polymers are divided into biological & nonbiological materials. Each is of great importance. Biological polymers like glycine, adenosine, lysine etc. form the very foundation of life and provide much of food on which man exists. Because of very high transparency and optical clarity, the polymers of nonbiological materials are used in a variety of applications such as laboratory and medical ware. Some polymers have outstanding good electrical properties. Some polymers are chemically inert. Styrene-butadiene copolymer is widely used for electrical insulation. Because of good electrical properties & low dielectric loss at very high frequency, polytetrafluoroethylene is used in television and radar. Polyvinylidene fluoride valves are used in chemical & nuclear industries.
1.4 POLYMER AND SOLVENT:

It is necessary to remove original interaction between the molecules of a species completely or at least, to reduce it, almost to a negligible extent, in order to reflect its characteristics in physical behaviour. Hence solutions of polymers in inert solvent such as tetrahydrofuran (THF) have been used to study molecular interaction between two polymers. The concentration of the polymers in tetrahydrofuran has been kept small.

1.5 INTERMOLECULAR FORCES:

Force of attraction binds different atoms together so as to form molecule. These intermolecular forces are basically electrostatic in nature. When atoms combine to form a molecule, their electrons rearrange themselves to achieve a stable configuration. This rearrangement of electrons gives rise to different types of bonds. The forces of attraction between molecules are responsible for the change in physical state. Internal pressures are quite large as compared to external pressures. Hence attractive forces of cohesion are significantly large.

(i) **Ionic bonds**:

These are very strong bonds amongst the polar bonds. They are formed due to electrostatic attraction between two stable ions produced by the transfer of an electron from one atom to another. By transfer of electron from one atom to another, both the atoms become stable ions.

(ii) **Covalent bonds**:

This bond is formed when two atoms achieve stability by sharing an electron pair, each contributing one electron to the pair. This bond accounts for the formation of molecules, in which the constituent atoms are of the same type. The required number of electrons can be attained by sharing electrons from neighbouring atoms.

(iii) **Co-ordinate bonds**:

This bond is formed when two atoms combine in such a way that both of the shared electrons are contributed by one atom only.

(iv) **Dipole - dipole forces**:

All the above mentioned (Primary) chemical bonds are formed by rearranging valency electrons from the outer region of the participating atoms into new spatial
distribution, which embrace both atoms. If the two atoms forming bond are dissimilar, the sharing of valency electrons is unequal. The electron distribution is not symmetrical and the bond has a definite electrostatic polarity, which arises because one atom is able to draw electron charge more strongly to itself than the other. This electrical effect is strong enough to constitute dipole. These dipoles are referred to as permanent dipoles. The molecules in which dipoles are permanent are called as polar molecules.

The forces between polar molecules are called as dipole-dipole forces. The force between polar-polar molecules is stronger than force between polar-nonpolar molecules. If the nonpolar molecule is brought near polar molecule, a dipole is induced in the nonpolar molecule.

(v) **Vander Waals' force**

The elements and compounds, in which such an electron transfer is not possible, these primary bonds can not be formed. In such a case bonds are formed by weak vander waals' forces. These bonds are known as molecular bonds. These bonds are formed due to attraction between the nucleus of one atom and the electrons of the other and vice versa.
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