CHAPTER – 1

(INTRODUCTION)
INTRODUCTION

1.1. GENERAL INTRODUCTION

Ultrasonics:

Ultrasonics is the technology of sound and science of acoustics. The frequency range of ultrasonic waves is greater than 20 kHz up to several MHz, which is beyond the audible limit. Low amplitude waves are more pronounced at frequencies between 2 to 10 MHz. The waves whose frequencies are lower than the audible limit are called infrasonics. The upper limit for gases is around 5 MHz and for liquids is 500 MHz. But, human ears do not respond to either of these frequencies. The ultrasonic technique is used for different investigations due to the following advantages:

- At higher frequencies, the high absorption coefficient values are easily measurable.
- Shorter wavelengths occur at higher frequencies so that plain wave conditions are more easily realized which are especially important for the smaller specimens.
- Frequencies associated with relaxation phenomena often fall within the ultrasonic range and therefore they can be easily focused.
- Less cost with efficiency comparable to other methods.

The study of acoustics had its beginning with the Greek philosopher Pythagoras in 600 BC. The foundation he laid for the use of stringed instruments is considered a milestone in the science of acoustics. It is believed that Galileo was the first to start the modern studies of acoustics. In 1638, he showed that pitch is associated with vibration, which was considered to be the second milestone in the
science of acoustics. He elevated the study of vibration to scientific standards by successful correlation of pitch with frequency of sound source. Investigations in high frequency waves did not emerge until nineteenth century.

The era of modern ultrasonics began only in the early 20th century with Langevin’s use of high-frequency acoustic waves and quartz resonators for submarine detection in 1917. From then on, slow but steady progress was made in the measurements of propagation constants of materials. Early landmarks included Pierce’s quartz-driven ultrasonic interferometer¹ in 1925 and the discovery in 1932 by Debye and Sears and also by Lucas and Biquard of the ultrasonic diffraction grating. An important event during 1930s was the pioneering work of Sokolov in 1934 on ultrasonic flaw detection.

Ever since, the field has grown enormously with wide applications in science, medicine and other areas. Graff² investigated physical, chemical and biological effects of ultrasounds on macromolecules, microorganisms and cells. Stokes³ made the first attempt in medical imaging using ultrasonics.

An ultrasonic velocity study provides a lot of information on molecular interactions. Ultrasonic wave propagation affects the physical properties of the medium and hence can furnish information on the liquid and liquid mixtures. Studies on ultrasonic velocity, density, viscosity, acoustic, thermodynamic, excess thermodynamic parameters and their deviations in binary systems have been the subject of many investigations in the recent years⁴–¹⁰. These investigations on different systems reveal specific interactions between the molecules of the component liquids.

An ultrasonic wave being transmitted through a substance is of two types. Each type causes a specific movement in the elements of medium and the paths that
these elements follow as they move in response to the wave are called their orbits. These orbits may be parallel to the line of propagation in which case the waves are called longitudinal waves. If the path followed by the elements is normal to the direction of propagation, the waves are called transverse waves or shear waves. Since liquids do not possess shear elasticity, transverse waves cannot exist in liquids. Rectilinear propagation is a characteristic exhibited by ultrasonic waves because of their short wavelength\textsuperscript{11,12}. The short wavelength of the ultrasonic waves is the factor that has been made possible the application of these waves in many cases.

The study of the propagation behaviour of ultrasonic waves in solids, liquids, liquid mixtures, electrolyte solutions, suspensions, polymers, soaps etc. is now rather well established as an effective means for examining certain physical properties of materials or medium, molecular interactions etc.\textsuperscript{13-16}. Ultrasonic waves with low amplitude have been used by many workers\textsuperscript{17-28} to investigate the structural and physico-chemical behaviour of pure liquids and liquid mixtures. It has been reported by many workers\textsuperscript{17,23} that, occurrence of complex formation can be explained successfully by excess parameters such as $U^E$, $\beta^E$, $L^E_f$ etc. The positive values of $U^E$ and negative values of $\beta^E$ show strong interactions occurring in liquid mixtures showing the possibility of complex formation\textsuperscript{28}. This occurs due to the formation of discrete groups of molecules arranged into specific geometric structures which are influenced not only by the shape of molecules but also by the mutual interactions occurring between them.

Lagemann and Dunbar\textsuperscript{29} pointed out the sound velocity approach for the qualitative estimation of interaction in liquids. A parallel measurement of sound velocity, density and viscosity of liquid mixtures allows one to obtain information
about their volume, compressibility, free length, internal pressure, acoustic impedance, enthalpy and changes in their properties. Complex formations, formation of hydrogen bond, Dipole – dipole, dipole- induced dipole interactions in solutions and their effect in physical properties of the mixture have received much attention.

Density and viscosity of liquid mixtures are required in most engineering calculations where fluid flow of mixture is an important factor. Moreover, knowledge of the dependence of densities and viscosities of liquid mixtures on composition is of great interest from a theoretical stand point since it may lead to better understanding of the fundamental behaviour of liquid systems. Knowledge of density and viscosity is essential in the design processes involving chemical separations, equipment design, solution theory heat transfer, fluid flow and molecular dynamics. Viscosity data are useful for testing theories and empirical relations such as Grunberg and Nissan, Tamura and Kurata, Hind et al., Katti and Chaudhr, Heric, etc for liquid mixtures.

The study of molecular interactions and the variations in these interactions due to structural changes have been carried out by various experimental techniques such as Infrared Spectroscopy technique, Nuclear Magnetic Resonance, Raman spectra and dielectric property measurements. But, the complete understanding of the nature of intermolecular and intramolecular interaction may not be possible by any single method. Ultrasonic methods have the added advantage of being less cost with efficiency comparable to other methods. Hence, a number of works have reported the study through ultrasonic method.

The molar sound velocity (R) and molar compressibility (W) are the two important parameters, which are widely used for the study of physico-chemical behaviour of liquid mixtures. The parameters are also called Rao’s constant (R) and
Wada’s constant (W) respectively. For many liquid mixtures, Rao’s empirical relation has been extensively used and verified by Chaudary et al.\textsuperscript{44} Wada’s constant is found to be useful in understanding the molecular interactions and structures of pure liquids and their solutions.

In chemical industry\textsuperscript{45,46} there exists a continuous need for reliable thermodynamic data of binary systems. Mixed solvents, rather than pure liquids find practical applications in many chemical and industrial processes. Their excess thermodynamic parameters enable us to understand the physico-chemical properties in a continuous manner.

An excess thermodynamic function denoted by superscript E is defined as the difference between the thermodynamic functions of mixing of a real mixture and the value corresponding to the ideal solution at the same conditions of temperature, pressure and composition. For an ideal solution all excess function are zero. For example the excess volume is given by

\[ V^E = V_{\text{real}}^M - V_{\text{ideal}}^M \]  

Excess functions may be positive or negative, their sign and magnitude representing the deviation from ideality. Both thermodynamic functions of mixing and excess functions become identical in respect of quantities where entropy does not appear. For example, the excess enthalpy \( H^E \) is identical with the enthalpies of mixture \( H^M \) and excess volume \( V^E \) is also identical with volume of mixing \( V^M \). Deviations from ideal behavior in terms of various properties like molar volume, adiabatic compressibility, viscosity etc. have been widely used for the structural variations and molecular interaction of liquid mixtures.

Several theories were proposed to study the ultrasonic velocities in binary and ternary mixtures. They are Flory’s theory\textsuperscript{47}, Jacobson’s free length theory\textsuperscript{48},
Schaaffs’ collision factor theory\textsuperscript{49}, Junjie’s empirical relation\textsuperscript{50}, Nomoto’s equation\textsuperscript{51}, Narasimhan and Manikam’s combined equation\textsuperscript{52}, Vandael ideal mixing relation\textsuperscript{53}, impedance relation\textsuperscript{54} and Rao’s specific velocity\textsuperscript{55}, Patterson theory\textsuperscript{56} and Flory-Patterson theory\textsuperscript{47,56,57}. Based on the additivity of internal energies, the sound velocity in a liquid mixture was determined by Kudriavstev\textsuperscript{58}. Theoretical evaluation of ultrasonic velocity in binary liquid mixtures and its correlation to study the molecular interaction has been successfully done in recent years\textsuperscript{59-69} using the above theoretical relations.

1.2. LITERATURE SURVEY

\textbf{a) Ultrasonic velocity, density, viscosity, Acoustic and Thermodynamic parameters- Intermolecular interactions:}

Rosal \textit{et al.}\textsuperscript{70} studied the viscosities and densities for binary mixtures of cresols in the temperature range 313.15–333.15K. The results showed mixtures containing o-cresol to be more fluid when compared to the pure liquids and positive viscosity deviations for m- and p-cresol mixtures. The results indicated an increase in the average degree of cross association of mixtures containing o-cresol.

Ultrasonic study of induced dipole-induced dipole interactions have been studied by Kannappan\textsuperscript{71} and Jaya Santhi\textsuperscript{72} in binary liquid mixtures of benzene, n-hexane, carbon tetrachloride and p-xylene with cyclohexane at 298K using ultrasonic velocity (U), density (\(\rho\)) and viscosity (\(\eta\)). They concluded that in the liquid mixture containing non-polar liquids, there exist weak induced dipole-induced dipole attractions. Further, they inferred that this type of intermolecular attraction depends on the polarizability of molecules of the components present in the mixture. They also studied the induced dipole-dipole interactions in binary liquid mixtures of pyridine, chlorobenzene, bromobenzene and nitrobenzene with p-xylene
at 298K using the measurement of ultrasonic velocity (U), density (\( \rho \)) and viscosity (\( \eta \)). They correlated the strength of dipole-induced dipole attractions with dielectric constant and dipole moment of the polar compounds.

Viscosities and refractive indices of binary mixtures of dimethylsulphoxide with some aromatic hydrocarbons at different temperatures have been studied by Anwar Ali et al.\(^7\) They calculated the deviations in both viscosity and molar refraction from the experimental data. They discussed the dependence of various thermodynamic parameters on composition of the mixtures, the effect of number and position of the methyl groups in these aromatic hydrocarbons on molecular interactions.

Density, viscosity, refractive index, surface tension and ultrasonic velocity of mixtures of para-anisaldehyde and chlorobenzene were measured as a function of mole fraction at temperatures of 303.15, 313.15 and 323.15K and at a pressure of 0.1 Mpa by Baskaran and Kubendran\(^7\). The ultrasonic velocity values were fitted to Jouyban-Acree model and Vandeal and Vangeel equation. The viscosity values were fitted to the models of McAllister, Grundberg and Nissan, Hind, Krishnan and Laddha and Jouyban-Acree. The excess values were correlated using the Redlich-Kister polynomial equation and they reported that excess molar volumes are found to be positive in the whole range of composition and at all the studied temperatures. The excess viscosities are found to be negative at all the studied temperatures and at any composition.

Thirumaran and Saradha Devi\(^7\) reported the experimental values of ultrasonic velocity, density and viscosity for the mixtures of 1-propanol, 1-butanol and 1-pentanol in p-xylene with nitrobenzene at 303K. Acoustical parameters are estimated from these data. They observed strong dipole-dipole interaction through
hydrogen bonding between nitrobenzene and 1-alkanols. They also noticed that the
donor-acceptor complexation exists between p-xylene and nitrobenzene molecules
with increase in adiabatic compressibility and intermolecular free length.

The negative values of excess adiabatic compressibility, excess free length as
well as excess free volume and positive values of excess acoustic impedance and
excess viscosity can be attributed to the strong interactions between unlike
molecules through hydrogen bonding as observed by Thirumaran and George\cite{76} for
the binary mixtures of m-cresols, o-cresols and p-cresols with N,N-Dimethyl
formamide (DMF) in CCl$_4$ at 303, 308 and 313K.

Narendra et al.\cite{77} calculated various acoustic and thermodynamic parameters
in the binary liquid mixture of cyclohexane and o-xylene for the whole mole fraction
range at the temperatures 303.15, 308.15, 313.15 and 318.15K and concluded that
there exist weak molecular interactions.

Densities and ultrasonic velocities were measured for binary mixtures
containing methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE) with o-
xylene, m-xylene and p-xylene at atmospheric pressure and at temperatures 288.15-
323.15K for the whole mole fraction range by Gonzalez-Olmos et al.\cite{78} They studied
the effect of ether in the aromatic environment in terms of steric hindrance and
oxygen group polar potency.

b) Excess thermodynamic parameters:

Reddy et al.\cite{79} studied thermodynamics of binary liquid mixtures of benzene,
carbon tetrachloride, carbondisulphide, p-xylene, m-xylene, o-xylene, toluene,
dioxan and tetralin with cyclohexane as common component. The agreement
between the calculated and experimental excess functions is found to be good in all
cases except in the system of cyclohexane and toluene.
Prasad et al.\textsuperscript{80} studied sound velocities and related properties of ternary mixtures of o-xylene. Excess values of adiabatic compressibility, intermolecular free length and free volume were used to investigate the molecular interactions in the ternary mixtures.

Pandey et al.\textsuperscript{81} studied the intermolecular interaction in the binary liquid mixtures of benzene + ethylene dichloride, benzene + carbon tetrachloride, acetone + chloroform, acetone + methyl iodide, acetone + carbondisulphide and benzene + p-xylene based on excess internal pressure values. They found that the excess internal pressure is a powerful tool for predicting intermolecular interaction in binary liquid mixtures. Pandey\textsuperscript{82} computed Van der Waals’ constant, excess internal pressure and sound velocity in the binary liquid mixtures benzene + p-xylene, benzene + p-dioxan and acetone + methyl iodide using Flory’s stastical theory. The agreement between experimental and theoretical values is found to be good.

Ultrasonic investigation of binary liquid mixtures of o-cresol with acetophenone, ethyl acetate and methyl ethyl ketone was carried out by Ganapathy et al.\textsuperscript{83} Rao’s constant, Wada’s constant and Van der Waal’s constant were computed and an analysis of these values suggested molecular association in these mixtures.

Govindappa et al.\textsuperscript{84} measured sound velocities in binary mixtures of 1-chlorobutane with benzene, toluene, o-xylene, m-xylene, p-xylene, chlorobenzene, bromobenzene and nitrobenzene. From the sound velocity and density data, excess compressibilities were derived and it was concluded that weak dipole-induced dipole interactions and dipole-dipole interactions were present in these systems.

Densities and viscosities of three binary systems, viz., p-xylene+m-xylene, p-xylene+o-xylene and m-xylene+o-xylene were measured by Lurdes et al.\textsuperscript{85} over
the complete concentration range and at the temperatures 273.15 and 303.15K. They also measured the above parameters for the ternary mixtures of the isomers and compared the viscosity data with McAllister equation.

Aralaguppi et al. calculated the excess molar volume, excess isentropic compressibility and excess molar refraction of binary mixtures of methyl acetoacetate (MAA) with benzene, toluene, m-xylene, mesitylene and anisole over the temperature range 298.15 – 308.15K.The excess molar volumes of all the mixtures are observed to be positive, suggesting the presence of weak dispersion-type molecular interactions. The excess isentropic compressibilities are negative for mixtures of MAA with benzene and toluene; however, for mixtures of MAA with mesitylene, anisole and m-xylene, both positive and negative values are obtained.

Ultrasonic studies in polar liquid mixtures of triethylamine with ethanol, n-propanol, n-butanol, phenol and o-cresol were carried out by Rajendran et al. The results suggested the existence of strong hydrogen bonding interaction between -NH2 and -OH groups.

Internal pressure and its excess values for the binary liquid mixtures of triethylamine with ethanol, n-propanol, n-butanol, phenol and o-cresol were evaluated by Rajendran. The results pointed out the fact that the excess internal pressure values provide useful information in the study of intermolecular interaction in binary liquid mixtures. Aralaguppi et al. studied the molecular interactions in the binary mixtures of methyl acetoacetate with benzene, toluene, m-xylene, 1,3,5-trimethylbenzene and methoxybenzene at 298.15K, 303.15K and 308.15K, based on the excess velocity and Gibb’s free energy values.

Ultrasonic studies of binary mixtures of 2-butoxyethanol with benzene, toluene, o-xylene, m-xylene, p-xylene, chlorobenzene, bromobenzene and
nitrobenzene at 303.15K were carried out by Prasad et al.\textsuperscript{90} The excess compressibility values were used to study the molecular interactions in these mixtures.

\textit{Sivaprasad and Venkateswarlu}\textsuperscript{91} determined ultrasonic velocity in the binary mixtures of 2-butoxyethanol with benzene, toluene, o-xylene, m-xylene, p-xylene, chlorobenzene, bromobenzene and nitrobenzene at 303.15K. The excess compressibility curve showed a positive deviation for the binary mixture of 2-butoxyethanol with three xylenes and a negative deviation for other mixtures. The positive deviation of excess compressibility revealed that structural effects predominated over the effects of complex formation between $\pi$ electrons of benzene ring and oxygen of 2-butoxyethanol and the negative deviation was attributed to the decrease in free length due to complex formation through charge transfer and dipolar association between the component molecules.

Kalra \textit{et al.}\textsuperscript{92} studied the molecular interactions in mixtures of quinoline with some aromatic hydrocarbons using ultrasonic, dielectric and viscometric methods. From the study, they concluded that strong specific interactions resulting from H-bond formation, closer molecular arrangement, donor acceptor interaction and self association of quinoline exists between unlike molecules.

The excess volumes for binary mixtures of 1-propanol or 2-propanol + benzene, + toluene, + o-xylene, + m-xylene, and + p-xylene have been measured by Kalra \textit{et al.}\textsuperscript{93} over the entire range of composition at 298.15 K. The excess volume curves for 1-propanol + toluene, + o-xylene and +p-xylene are sigmoids. For other mixtures the $V^E$ values are observed to be positive over most of the concentration range. For the system 2-propanol + benzene they observed the positive values of $V^E$ over the entire range of composition.
Densities and refractive indices are measured by Jose and Concepcion\textsuperscript{94} for binary mixtures of 1-hexane+o-xylene, +m-xylene, +p-xylene and +ethylbenzene over the entire composition range at 298.15K. They calculated the excess volumes and molar refraction deviations from them. The refractive indices are compared with the predictions of the Lorentz-Lorentz, Goldstone-Dale and Arago-Biot equations. The excess molar volumes are observed to be negative for all the mixtures. This may be attributed to interactions between the π electrons of the aromatic hydrocarbons and π electrons of the olefin group. Also they observed the increase in values of excess molar volume as the size of substituents on the benzene ring increases. They observed the positive deviations of molar refraction in the mixtures of 1-hexane with o-xylene, or p-xylene or ethylbenzene and negative deviations in the system, 1-hexane + m-xylene. The Goldstone-Dale relation gave best results than the Lorentz-Lorentz equation.

Chang et al.\textsuperscript{95} measured the densities of binary mixtures of m-cresol + m-xylene and m-cresol + tetralin at the temperatures of 298.15, 323.15 and 348.15K and pressures up to 30 MPa over the entire range of composition. They also calculated the isothermal compressibility and excess volumes of the mixtures and they found that the excess volumes of the mixture m-cresol + m-xylene are negative and those of m-cresol + tetralin are positive.

Viscosities and densities of dilute solutions of glycerol trioleate + chloroform at 10, 15, 20, 25 and 30°C and of glycerol trioleate +octane, +p-xylene, +toluene at 20, 25, 30, 35 and 40°C were measured by Exarchos et al.\textsuperscript{96} They observed the positive values in excess volumes for glycerol trioleate + chloroform system and negative values for the other systems over the entire range of mole fraction. The
results are discussed on the basis of specific interactions between the components of the mixtures.

The deviations in viscosity of ternary mixtures of tri-n-butyl phosphate + benzene + o-xylene were calculated by Swain et al.\textsuperscript{97} by measured values of viscosity and density at 30, 35, 40 and 45°C. The deviations were fitted to Redlich-Kister equation.

The densities in the temperature range 288.15 to 308.15K and the viscosities in the temperature range 293.15 to 308.15 K were measured by Moumouzias et al.\textsuperscript{98} for the binary systems γ-butyrolactone + o-xylene and m-xylene. They correlated the viscosity data with Heric, McAllister and Hind-McLaughlin-Ubbelohde equations. Viscosity deviations and excess volumes were calculated and found to be negative over the whole composition range. They concluded that the negative excess molar volumes may be due to different sizes and different geometries of the unlike molecules.

Densities, viscosities and refractive indices at 298.15, 303.15 and 308.15 K and speeds of sound at 298.15K were determined by Jyothi et al.\textsuperscript{99} for the binary mixtures of ethyl chloroacetate + benzene, toluene, p-xylene, mesitylene and anisole. By using the experimentally measured values they calculated the excess molar volume ($V^E$), deviations in viscosity ($\Delta\eta$), molar refraction ($\Delta R$), speed of sound ($\Delta u$) and isentropic compressibility ($\Delta k_s$).

Satyanarayana Rao et al.\textsuperscript{100} measured the densities, viscosities and ultrasonic velocities in binary mixtures of o-chlorophenol, o-cresol, m-cresol with N,N- diethyl acetamide at 308.15, 313.15, 318.15 and 323.15K over the whole composition range. By using these data, they evaluated the excess volume ($V^E$), excess viscosity ($\eta^E$), excess compressibility ($\beta^E$), excess inter-molecular free length ($L_f^E$) and
Grunberg Nissan parameter ($d^1$). They observed the negative values of $V^E$ for $o$-chlorophenol + N,N-diethyl acetamide system and $m$-cresol+N,N-diethyl acetamide system at all temperatures but for o-cresol +N,N-diethyl acetamide the $V^E$ values were observed to be positive at lower mole fraction of o-cresol and increase with increase in temperature. Also they observed the negative values of $\beta^E$ and positive values of $\eta^E$ for all the systems over the whole composition range.

Excess volume, excess compressibility and deviation in viscosity of binary liquid mixtures of 3-pentanone + ethylbenzene and 3-pentanone + o-xylene at temperatures 293.15, 303.15 and 313.15K over the whole composition range have been studied by Katyal et al.\textsuperscript{101} using the experimentally measured values of densities, viscosities and ultrasonic velocities. They observed the negative deviations in viscosity over the entire composition range for the two systems, and concluded that the negative values of excess volume and deviation in viscosity for both the systems indicate the predominance of dipolar forces when compared to other interactions.

Excess molar volume ($V^E$), excess isentropic compressibility ($\beta^E$) etc., were calculated from the measured values of density, dynamic viscosity, speed of sound in binary mixtures dibutyl ether + benzene, or toluene, or p-xylene at different temperatures over the whole composition range and at atmospheric pressure by John and Sastry\textsuperscript{102}. The viscosities values were correlated with semi empirical relations. They found that speed of sounds calculated using Nomoto’s equation were found to be close to the experimental values for the three mixtures.

Lien et al.\textsuperscript{103} measured the excess molar enthalpies ($H^E$), for the binary mixtures of dimethylcarbonate with o-xylene, m-xylene, p-xylene, ethylbenzene or ethyl benzoate by using a flow-type isothermal microcalorimeter at 298.15K under
atmospheric pressure. For the entire range of composition they observed the positive values of $H^E$.

Densities for binary mixtures of isopropyl ether + o-xylene, + m-xylene, and + p-xylene are determined at 298.15 K by Gangfeng et al.\textsuperscript{104} They also measured the surface tensions for the above binary mixtures by the pendant-drop method at 298.15 K and calculated the excess molar volumes and deviations in surface tension. For all the mixtures they observed negative values for $V^E$ and negative values for $\delta\sigma$. The $V^E$ values follow the order m-xylene > p-xylene > o-xylene and $\delta\sigma$ is of the order of o-xylene < m-xylene < p-xylene.

Excess molar volumes and deviations in viscosity of binary mixtures of p-xylene with cyclohexane, n-heptane, n-octane etc., at 303.15K and 323.15K and atmospheric pressure have been studied by Yang et al.\textsuperscript{105} The computed values were fitted to the Redlich-Kister equation to derive the coefficients and to estimate the standard error values. The results were discussed in terms of intermolecular interactions.

Yang et al.\textsuperscript{106} found the experimental values of density and viscosity at 303.15 and 323.15 K for the binary mixtures sulfolane + benzene, toluene, ethylbenzene, p-xylene, o-xylene and m-xylene. From these data, they calculated the excess volumes and deviations in viscosity and they found that they are negative for all the mixtures. The results were discussed in terms of intermolecular interactions.

Densities and volumetric properties of o-xylene, m-xylene, p-xylene + dimethyl sulfoxide at temperatures 293.15, 303.15, 313.15, 323.15, 333.15, 343.15, 353.15 K and at atmospheric pressure are measured by Haijun et al.\textsuperscript{107} They calculated the excess molar volume and excess partial molar volumes and they found that in all the systems $V^E$ values increase with rising temperature and also
found that p-xylene is the most favorable one to form close packing with dimethyl sulfoxide.

Sukhmehr Singh et al.\textsuperscript{108} calculated the excess volume, excess compressibility and deviation in viscosity from the measured values of viscosity, density and speeds of sound of the binary mixtures of 4-methylpentane-2-one with o-xylene, m-xylene, p-xylene and isopropylbenzene at 298.15K over the whole composition range. They observed the negative deviations for systems containing o-xylene and p-xylene for the entire composition range, whereas positive deviations for the systems containing m-xylene and isopropylbenzene. They concluded that the large negative deviations for the systems containing o-xylene and p-xylene are due to the strong dispersion forces existing in these systems and the observed negative volumes can be attributed to an ordering of molecules in the mixture.

Excess enthalpies ($H^E$) of the binary mixtures containing poly (propylene glycols) of different molecular masses + benzyl alcohol, or + m-cresol, or + anisole were determined by Fabio and Stefano\textsuperscript{109} using a flow micro calorimeter at 308.15K and at atmospheric pressure. The results were explained based on molecular interactions and of regular solution model.

Free volume, internal pressure and enthalpy are calculated for the binary mixtures of o-chlorophenol with ethyl benzoate, anisic aldehyde and acetonitrile at 303.15, 308.15, 313.15 and 318.15 K over the entire range of composition from the measured values of ultrasonic velocity, density and viscosity by Rama Rao et al.\textsuperscript{110} They also calculated the excess values of free volume, internal pressure, enthalpy and Gibb’s free energy of activation. Based on the negative values of $V_f^E$ and positive values of $\pi^E$ and $H^E$ they concluded that complex formation between the hetero molecules of the mixture.
The densities of binary mixtures of tetrahydrofuran (THF) with benzene, toluene, o-xylene, m-xylene, p-xylene and mesitylene including pure liquids are measured by Anil Kumar Nain\textsuperscript{111} over the entire composition range at temperatures 278.15 to 318.15 K and atmospheric pressure. From the experimental data he calculated the excess molar volume ($V_m^E$), partial molar volume and excess partial molar volume at infinite dilution. He observed the negative values of $V_m^E$ for all the mixtures over the whole composition range at each temperature studied, except for THF + mesitylene. It is observed that the $V_m^E$ values depend upon the number and position of the methyl groups in these aromatic hydrocarbons.

Changsheng et al.\textsuperscript{112} calculated the excess molar volumes and viscosity deviations of binary mixtures of m-cresol and p-cresol with ethylene glycol and methanol at different temperature and atmospheric pressure over the entire composition range. The excess molar volumes for binary systems, m-cresol + ethylene glycol, m-cresol + methanol, p-cresol + ethylene glycol, p-cresol + methanol are observed to be negative over the whole composition range and at all measured temperatures. The deviations of viscosity for m-cresol + ethylene glycol, p-cresol + ethylene glycol are observed to be positive and the values for m-cresol + methanol and p-cresol + methanol are negative. They concluded that when one solution with higher viscosity is mixed with that of lower viscosity solution to form a binary mixture, usually the viscosity deviations are negative and the curve of the viscosity deviation on mole fraction is skewed to the higher viscosity solution.

While studying the excess compressibility ($\beta^E$) and deviations in viscosity ($\Delta\eta$) in binary mixtures of benzene, toluene, o-xylene, m-xylene, p-xylene and mesitylene with anisole at 288.15 to 303.15K, Jasem et al.\textsuperscript{114} reported that the $\beta^E$ and
Δη values are negative for all the systems and for the entire composition range. The experimental viscosity data were fitted to several semi-empirical relations.

Jasem A. Al-Kandary et al.115 studied the dependency of intermolecular interaction on the alkyl substitution on benzene ring in binary mixtures, anisole + benzene, or toluene, or o-xylene, m-xylene, or p-xylene, or mesitylene over the entire range of mole fraction at temperatures 288.15, 293.15, 298.15 and 303.15K using the excess molar volume and molar refraction deviation. They observed the positive deviation of $V^E$ for anisole + mesitylene and negative for anisole + benzene, or toluene, or xylene isomers.

Ali and Nain116 measured the densities and ultrasonic speeds of pure dimethyl sulfoxide (DMSO), benzene, toluene, o-xylene, m-xylene, p-xylene, mesitylene and those of their binary mixtures with DMSO as common component at different temperatures. A number of parameters are calculated and based on the variation of these parameters with composition and temperature they concluded that the interactions are in the order of benzene > toluene > p-xylene > m-xylene > o-xylene > mesitylene.

Anil Kumar Nain117 calculated the excess molar compressibility, deviation in ultrasonic velocity and deviation in viscosity of binary mixtures of tetrahydrofuran (THF) with some aromatic hydrocarbons at temperatures from 288.15 to 318.15 K. The variation of these parameters with composition and temperature of the mixtures were discussed in terms of molecular interactions in these mixtures. The effect of position and number of the methyl groups in these aromatic hydrocarbons on the molecular interactions in these mixtures were also discussed.

Baskaran and Kubendran118 measured the density and viscosity of the binary mixtures of anisaldehyde with benzene at 303.15, 313.15 and 323.15K. From these
results, they calculated the excess parameters and found that the viscosity deviations are negative for all the mole fractions at all the temperatures studied. In addition, they found that the values of excess molar volumes are negative at low temperatures and positive at higher temperature, which may due to weak intermolecular forces.

Yang et al. \(^{119}\) calculated the excess molar volumes and viscosity deviations in binary liquid mixtures N-formylmorpholine (NFM) with p-xylene, m-xylene and o-xylene from the experimental values of density and viscosity at several temperatures and atmospheric pressure over the whole range of mole fractions. The results were fitted to the Redlich-Kister equation. They observed the negative values for excess molar volume and deviation in viscosity and the deviation in viscosity values are less negative with increase in temperature and excess molar volume values are more negative with increasing temperature.

The speed of sound and densities of binary mixtures of Butyl acetate with aromatic hydrocarbons over the entire mole fraction range were measured at 308.15K by Deshwal et al. \(^{120}\) From the experimental values of \(u\) and \(\rho\), the excess isentropic compressibility values were calculated and discussed the variation of this parameter with composition in terms of molecular interactions in these mixtures. The negative \(K_s^E\) values for all the binary mixtures except for the butyl acetate + benzene system suggested that the dipole-induced dipole interactions between polar ester and aromatic hydrocarbons are quite significant.

Anwar Ali and Firdosa Nabi \(^{121}\) studied the intermolecular interactions of binary liquid mixtures styrene with m-, o-, or p-xylene at the temperatures 298.15, 303.15, 308.15 and 313.15K. From the experimental data of ultrasonic speeds (\(U\)) and densities (\(\rho\)), the excess volume, deviations in isentropic compressibility, acoustic impedances and refractive indices were calculated. The variation of these
parameters with the composition suggested the stronger interactions between styrene and xylene molecules follow the sequence: p-xylene > o-xylene > m-xylene and also the order of favorable accommodation of the component molecules into each others structures. They concluded that π...π interactions between styrene and p-xylene molecules and also their accommodation into each others structure are maximum when the second methyl, -CH₃ group is at p-position, followed by o-xylene in which –CH₃ group is at o-position and the interaction is least in case of m-xylene in which –CH₃ group is at m-position. This suggests that the position of –CH₃ groups on the aromatic rings plays a substantial role in deciding the magnitude of Vₑ and ΔKₛ, and hence the above order of interaction between the component molecules of the mixture.

Rathnam et al.¹²² studied the molecular interactions in binary liquid mixtures of methyl formate with o-, m- and p-xylenes using viscosity data at 303.15K. The ability of various single parameter and two-parameter empirical models to predict viscosities of the mixtures was also studied. They observed the negative values of deviation in viscosity (Δη), positive values of excess Gibbs free energy of activation of flow (ΔG*ₑ) and both positive and negative values of deviation in molar refractive index (ΔR) over the entire range of composition for all the studied systems and they also observed that McAllister equation with two adjustable interaction parameters yields better results.

The ultrasonic velocity, density and viscosity values were measured by Thirumaran and Sarada Devi¹²³ for the mixtures of 1-alkanols in p-xylene with nitrobenzene at 303K. The acoustical parameters like adiabatic compressibility (β), free length (Lₜ) free volume (Vₜ), internal pressure (πᵢ) and acoustic impedance (Z) were calculated from the experimental data. Some excess parameters were also
evaluated and observed the existence of strong dipole-dipole interaction through hydrogen bonding between nitrobenzene and 1-alkanols whereas donor-acceptor complexation between p-xylene and nitrobenzene molecules.

Sastry et al. measured the experimental densities, dynamic viscosities and velocity of sound of thirty six binary mixtures of esters over the whole composition range at atmospheric pressure and temperatures 298.15 to 313.15 K. They calculated the excess molar volumes, excess isentropic compressibilities, deviation in relative permittivities and the results were fitted to Redlich-Kister type equation. The qualitative analysis of various functions revealed that i) weak electron donor-acceptor complexes predominate in the mixtures of esters with halogenated and nitrated benzene. (ii) esters lose their dipolar association in presence of inert and unlike n-hexane and (iii) Specific but weaker n…π type interactions predominate in binary mixtures of esters + aromatic organic solvents.

The nature and strength of the interaction in the binary systems of cyclohexanone with o- and p-cresol at 303.15K were discussed by Uvarani and Sivapragasam from the properties of excess parameters. They observed the negative values of and at all concentrations and concluded that there exist intermolecular interactions between the components.

Parveen et al. measured the ultrasonic velocity, density, viscosity and refractive indices of binary liquid mixtures of tetrahydrofuran (THF) with methanol and o-cresol over the entire composition range at temperatures 293, 303 and 313K. Using these experimental data, they calculated some thermo-acoustical parameters and excess parameters. They observed the negative values of and in the binary mixtures of THF + o-cresol over the entire composition range and they also observed that the absolute values of increase as the temperature increases,
suggesting an increase in intermolecular interaction between unlike molecules due to thermal energy. The negative values of $V_{E}^{f}$ suggested the existence of strong dipole-dipole type of interaction through hydrogen bonding between oxygen atom of THF and hydrogen atom of hydroxyl group in o-cresol.

Yasmin et al.\textsuperscript{127} evaluated the excess thermo acoustical properties of binary liquid mixtures containing o-cresol at temperatures 293, 303 and 313K for the whole mole fraction by using the experimentally measured ultrasonic velocity, density and viscosity. The observed values of the excess parameters plotted against the mole fraction of THF have been explained on the basis of intermolecular interaction suggesting strong interaction in THF + o-cresol than in THF + methanol.

Gonzalez et al.\textsuperscript{128} studied the excess thermodynamic properties like excess molar volumes and excess isentropic compressibility of the binary liquid mixtures containing cycloalkanes with o-xylene, m-xylene, p-xylene and mesitylene at temperatures 298.15 and 313.15 K over the entire mole fraction range at atmospheric pressure. The excess properties were fitted to Redlich-Kister polynomial equation.

Narendra et al.\textsuperscript{129} calculated various excess acoustic and thermodynamic parameters in binary liquid mixtures at different temperatures. Based on the deviations, they concluded that there exist weak interactions between the molecules of the component mixtures.

The densities of binary mixtures of butyl acrylate (BA) with benzene, toluene, o-xylene, m-xylene, p-xylene and mesitylene over the entire mole fraction range were measured by Nain et al.\textsuperscript{130} at the temperatures 288.15 to 318.15K at atmospheric pressure. The excess volumes were calculated from the experimental data and observed that for all the mixtures, the $V_{E}^{m}$ values are negative at each
temperature except for BA+ mesitylene. They concluded that the results indicated the presence of specific interactions between BA and aromatic hydrocarbon molecules.

Physical properties of speeds of sound, densities and refractive indices were determined experimentally and their derived and excess properties like excess molar volumes, excess compressibility of the binary systems containing cycloalkanes with aromatics at the temperatures of 298.15 and 313.15K and at atmospheric pressure were determined over the whole composition range by Gonzalez et al. All the studied excess properties were satisfactorily fitted to the Redlich-Kister equation.

Densities, speeds of sound and refractive indices of binary mixtures of decan-1-ol with o-cresol, m-cresol, p-cresol and anisole were measured by Bhatia et al over the entire range of mole fraction from the temperature of 298.15 to 308.15 K and at a pressure of 0.1 MPa. The experimental values were used to calculate the excess molar volumes. They observed that the excess molar volume values are negative over the entire composition range for the binary mixtures of decan-1-ol with o-cresol and p-cresol and give an s-shaped curve with o-cresol at the high mole fraction region of o-cresol. The excess molar volume is positive for the mixture of decan-1-ol and anisole.

Densities and speed of sound of binary liquid mixtures of 1-nonanol with o-cresol, m-cresol, p-cresol and anisole were measured by Bhatia et al.133 over entire range of composition at T= 293.15 and 313.15K and at atmospheric pressure. Using these data, they calculated the excess molar volume ($V^E$), excess free volume ($V^{E_f}$), excess isentropic compressibility ($K^E$) and deviation in speed of sound ($\Delta u$). The $K^E$ values were observed to be positive for the 1-nonanol + anisole mixture and negative for the mixtures of 1-nonanol with isomeric cresols over the whole
composition range. They concluded that the negative values of $K^E$ are due to the strong intermolecular interactions.

c) Theoretical evaluations:

Islam and Quadri\textsuperscript{134} observed that the average absolute percentage relative deviation values are maximum for the p-chlorophenol + DMSO systems in respect of two relations and two theories and minimum for the o-cresol + DMSO systems in respect of the relations and theories excluding the ideal mixing relation. In case of ideal mixing relation, phenol + DMSO system exhibited minimum deviation and they concluded that these results not only show the feasibility of these but also envisaged the rising deviation with increasing non ideality in the mixture.

Pandey \textit{et al.}\textsuperscript{135} evaluated ultrasonic velocity using Free length theory (FLT), Collision factor theory (CFT), Nomoto’s relation (NR) and Ideal mixing relation (IMR) in the binary mixtures of 1,1,2,2-tetrachloroethane with benzene, toluene, p-xylene, acetone and cyclohexane at 298.15 and 318.15K, and showed that IMR gives the minimum deviation for all the systems except acetone.

The experimental values of ultrasonic velocities with theoretical values of Nomoto, Van Dael ideal mixing relation and Schaffs collision factor theory in binary liquid mixtures chlorobenzene+ bromobenzene, toluene+aniline and toluene+p-xylene are compared by Pandey \textit{et al.}\textsuperscript{136} at 303.15K up to 200MPa. For polar-polar liquid system the collision factor theory provides best results followed by Nomoto’s relation and ideal mixing relation. However in case of polar-nonpolar and nonpolar-nonpolar mixtures, both Nomoto’s relation and an ideal mixing relation give almost identical results, but the collision factor theory gives the best results.
The measurement of ultrasonic velocity and density was made by Rastogi et al.\textsuperscript{137} for the ternary mixtures of benzyl chloride and bromobenzene with o-cresol in a non-polar solvent, carbon tetrachloride at various concentrations at the temperatures 30, 40 and 50°C. Various physical parameters such as adiabatic compressibility, intermolecular free length and their excesses in mixtures were evaluated and found that weak molecular interactions exist in these mixtures. The experimental values have been compared with theoretically estimated velocities using Nomoto relation and also ideal mixing relation. By using the data, they concluded the complex formation.

The ultrasonic velocities in binary liquid mixtures of m-xylene with 1-propanol, 1-butanol and 1-pentanol at the temperature of 303.15K were computed theoretically at different mole fractions from Jacobson’s free length theory and Schaff’s collision factor theory by Prabhavathi et al.\textsuperscript{138} The results pointed out that both the theories give a satisfactory estimate of the measured property. However, velocities of sound predicted by FLT method are closer to experimental values.

Rama Rao et al.\textsuperscript{139} compared the ultrasonic velocities evaluated from Nomoto’s relation, Van Deel ideal mixing relation, Impedence relation, Rao’s specific velocity relation and Junjie’s theory with the experimentally measured ultrasonic velocity values in three binary liquid mixtures of o-chlorophenol as component with ethylbenzoate, anisicaldehyde and acetonitrile at 303.15, 308.15, 313.15 and 318.15 K. They found the good agreement between Nomot’s relation and experimental ultrasonic velocities. The results were explained in terms of intermolecular interactions occurring in these binary systems.

The speeds of sound in binary mixtures of benzene with toluene, o-xylene, m-xylene, p-xylene and mesitylene using CFT and FLT were measured by Jaseem et
From their results they concluded that CFT of Schaff’s is more appropriate for prediction of speeds of sound data for these mixtures.

Nomoto, Junjie, CFT and Florry’s theory were applied for evaluating the ultrasonic velocity theoretically in binary mixtures of tetrahydrofuran with methanol and o-cresol by Parveen et al. The comparison of theoretical and experimental results provided better understanding about the validity of various thermodynamic, empirical, semi empirical and statistical theories. They used these values to correlate with the experimental findings to know the thermodynamics of the mixtures and found that CFT relation is more suitable for the two mixtures.

Narendra et al. evaluated the ultrasonic velocities theoretically using different theories and compared the results with the experimental values to know the interactions between the molecules of the binary mixture containing cyclohexane and o-xylene.

Santhi et al. measured the ultrasonic velocities and densities of binary liquid mixtures of dimethyl sulphoxide (DMSO) with phenol, o-cresol, m-cresol, p-cresol and p-chlorophenol at 318.15K over the whole mole fraction range. Using different theories/relations they evaluated the ultrasonic velocity and correlated the experimental values with theoretical values. Nomoto’s relation gave a satisfactory evaluation of sound velocity in binary mixtures. The positive values of $\alpha$ in case of all the systems clearly indicated the existence of strong tendency for the formation of association of mixtures to form complexes through hydrogen bonding. They observed the greatest interaction between p-chlorophenol and DMSO and the weakest interaction between o-cresol and DMSO. This result may be due to the low Pka value of p-chlorophenol than that for other phenols used in this study.
1.3. NATURE AND SCOPE OF THE PRESENT WORK:

Knowledge of excess properties of binary mixtures has got relevance in theoretical and applied areas of research because such results are used in design process, in chemical and petrochemical processes. The behavior of liquid mixtures utilized can be predicted from the excess properties and the extent of deviations.

Interaction studies in a system comprising of arenas (aromatic hydrocarbons) have attracted the attention of researchers in recent years because as these systems find applications in the studies of polymer phase diagrams and the preferential interaction of polymers in mixed solvents. Phenols are widely used for making explosives and dyes. The volumetric, viscometric, acoustic and thermodynamic studies in mixtures have been used for understanding intermolecular interactions by many researchers for interpreting different types of interactions viz., dipole-dipole, dipole-induced dipole in polar-polar and polar-non polar systems. Increasing use of anisaldehyde, arenes and cresols in many industrial processes have greatly stimulated the need for extensive information on the acoustic and transport properties of these liquids and their mixtures.

Commercial use of anisaldehyde includes in the preparation of vanilla, spices, apricot, butter, cinnamon and chocolate, caramel, cherry, walnuts, mint flavor. It can also be used for daily flavor and flavors. Also for the manufacture of anti-microbial drugs, in Pharmaceutical industry.

Xylene is often used as a solvent and in the printing, rubber and leather industries. It is used a thinner for paints and in paints and varnishes. It is used as a cleaning agent for steel and silicon wafers and chips.

Cresol solutions are used as household cleaners and disinfectants and also used as antiseptics in surgery. Cresols are found in wood and many foods.
The above salient features of these liquids have motivated the author to carry out the present study of binary liquid mixtures of anisaldehyde with arenes and cresols at different temperatures (303.15, 308.15, 313.15 and 318.15) K. The present work deals with the measurement of Ultrasonic velocity, density, viscosity and evaluation of related parameters in the following binary liquid systems at different temperatures.

System 1: anisaldehyde + o-xylene
anisaldehyde + m-xylene
anisaldehyde + p-xylene
anisaldehyde + mesitylene

System 2: anisaldehyde + o-cresol
anisaldehyde + m-cresol
anisaldehyde + p-cresol

The data obtained can be used to understand intermolecular interactions between the unlike molecules and to test the theories of solutions. The departure of these results from ideal behaviour can be explained in terms of differences in size and shapes, position of methyl groups and dipole-dipole interactions between different component molecules.
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ANISALDEHYDE (C₈H₈O₂)

P-anisaldehyde commonly known as anisaldehyde is a clear colourless liquid with a strong aroma. Its boiling point is 248°C. It is found in anise. It is in similar in structure to vanillin. It is used as an intermediate in the synthesis of other compounds important in pharmaceuticals and perfumery. A solution of p-anisaldehyde in acid and ethanol is frequently used to stain thin layer chromatography plates.

Structure of anisaldehyde

O-XYLENE (C₈H₁₀):

It is a clear, colourless liquid and an aromatic hydrocarbon, based on benzene with two methyl substituents bonded to adjacent carbon atoms in the aromatic ring (the ortho configuration). It is an isomer of m-xylene and p-xylene.

α-Xylene is largely used in the production of phthalic anhydride, a small amount is also used in solvent applications and to make bactericides, soybean herbicides and lubricating oils. It is generally extracted by distillation from a mixed xylene stream in a plant primarily designed for p-xylene production. Its boiling point is 144 °C.
The other name of o-xylene is 1, 2-dimethylbenzene. The specific gravity is 0.88 and viscosity is 0.812 cP at 20 °C. Creates irritation in case of skin or eye contact. It may be toxic to kidneys, liver upper respiratory tract, skin, eyes, central nervous system (CNS). Repeated or prolonged exposure to the substance results in damage to the target organs.

m-XYLENE:
m-XYLENE is largely used in the manufacture of isophthalic acid, which is used as a copolymer to alter the properties of polyethylene terephthalate (PET) making PET more suitable for the manufacture of soft drinking bottles. It is also used as a raw material in the manufacture of 2,4-and 2,6-xylidine as well as a range of smallervolume chemicals.

p-XYLENE:
The p stands for para, identifying the location of the methyl groups as across from one another. P-xylene is used on a large scale for the manufacture of terephthalic acid for polyester. Its polymer is known as parylene. P-xylene is produced by catalytic reforming of naptha and separated in a series of distillation, adsorption or crystallization and reaction processes from m-xylene, o-xylene and ethylbenzene. Its melting point is the highest among this series of isomers.

Structures of o-xylene, m-xylene and p-xylene
CRESOLS (C₇H₈O):

In its chemical structure, a cresol molecule has a methyl group substituted onto the benzene ring of a phenol molecule. There are three forms of cresols that are only slightly different in their chemical structure. Cresol solutions are used as household cleaners and disinfectants. Cresols are found in many foods and in wood and tobacco smoke, crude oil, coal tar and in brown mixtures such as creosote, cresolene and cresylic acids, which are wood preservatives.

- **o-cresol** is a colourless liquid. Its boiling point is 191.5°C.

- **m-cresol** is a colourless liquid to yellowish liquid. Its boiling point is 202.8°C. It can be used as a solvent for dissolving polymers, most notably the conducting polymer polyaniline. When polyaniline is cast from a solution of m-cresol or a polyaniline film is exposed to m-cresol vapour the conductivity is higher than a polyaniline film cast without the presence of m-cresol.

- **p-cresol** is a colourless liquid. Its boiling point is 201.8°C. It is a major component in pig odor. It is a human odor attractive to female mosquitoes.