## PREFACE

The study of molecular interactions is a fascinating world of research field. Many researchers are still attracting to this field of research because of extensive applications and enormous uses of liquid mixtures in the industries. Physico chemical measurements are very useful in chemical and food processing, material testing, under water range cleaning etc. Ultrasonic study has wide range of applications in the fields of physics, chemistry, biology and medicine. Liquid-liquid mixtures are very useful in industries and laboratories than the individual components since they improve some characteristics like density, viscosity, surface tension, boiling points etc. The intermolecular interactions play a vital role in determining the absolute values of different physical properties of liquid mixtures when the individual components are mixed in different compositions. Based on the molecular structures, nature of solvents and sizes of the component molecules, weak or strong interactions are observed.

Many research workers have made efforts on different mixtures to understand the type of interactions by mixing the constituent components in different compositions. Thermodynamic properties are necessary for the development of thermodynamic models and optimized processes of the chemical, petrochemical, pharmaceutical, and other industries. In addition, extensive information about structural phenomena of mixtures is of importance in the development of theories of the liquid state and predictive methods.

**Diethyl malonate (DEM)** is the diethyl ester of malonic acid. It occurs naturally in grapes and strawberries. It has an apple-like odour, and is used in perfumes. It is used for the synthesis of compounds such as barbiturates, artificial flavourings, vitamin $B_1$, and vitamin $B_6$. It is an important solvent in paints and perfume industries. It is a colorless pleasant smelling liquid. It is sparingly soluble in water and easily soluble in many organic solvents. Diethyl molanate contains active methylene group ($-CH_2-$) in the middle of the malonic part of the molecule, which is neighbored by two carbonyl groups (-C=O)-). It is used as a solvent for many cellulose derivatives and natural and synthetic resins.

The literature survey reveals that much work has been done with different mixtures but there is no work in the combination of diethylmalonate with 1- alkanols, 2- alkoxyethanols, amides and benzene and monosubstituted benzenes was found. And the mixtures in these combinations find many applications in industries. Hence

these systems have been selected for the study of molecular interactions. In the present investigation, the main focus is on the study of thermodynamic, ultrasonic and viscometric properties by measuring the ultrasonic speeds, densities and viscosities of the binary mixtures of diethyl malonate over the complete composition range at temperatures of 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure.

From these measured values, several acoustic and thermodynamic properties like molar volume(V), adiabatic compressibility (βad), inter molecular free length ($L_f$), specific acoustic impedance (Z), enthalpy (H) and Gibbs free energy (G) are computed. Further deviation/excess properties of acoustic, thermodynamic and transport parameters such as excess molar volume ($V^E$), deviation in adiabatic compressibility (Δβad), excess intermolecular free length ($L_f^E$), excess specific acoustic impedance ($Z^E$), excess enthalpy ($H^E$), excess Gibbs free energy ($G^E$), deviation in viscosity (Δη) and excess speed of sound ($U^E$) are evaluated from the above calculated parameters. The calculated deviation and excess functions have been fitted to the Redlich–Kister type polynomial equation, and their corresponding standard deviations are also evaluated. The variations of these functions with composition and temperature have been used to explain the nature of the interaction between the component molecules of the mixtures.

The molecular interactions between the unlike molecules of the binary liquid systems under investigation, with special reference to hydrogen bonding and dipole–dipole interactions of these mixtures are studied. Further, the experimental data of these binary mixtures is used to verify the applicability of empirical relations of Nomoto, Impedance relation, Van Dael and Vangeel, Junjie's and Rao's specific velocity equation for ultrasonic velocity and Grunberg–Nissan, Katti–Chaudhri, Heric–Brewer, McAllister (four body model) and Hind *et al.* models for viscosity. The interactions observed are verified with the support of FT-IR data.

For the sake of convenience, the thesis entitled ***"Evaluiation of molecular interactions in certain binaries of diethyl malonate through thermo physical and spectroscopic properties at different temperatures"*** has been divided into nine chapters for simple understanding.

**Chapter-1** gives general introduction to molecular interactions and types of molecular interactions, acoustic, volumetric and transport properties of binary liquid mixtures. Experimental data of physical properties in liquid mixtures are required for a full understanding of their thermodynamic properties, as well as for use in chemical

engineering industry. A thorough literature survey is made and the findings are reported in this chapter, selection of solvents for the study is presented in the continuation of literature survey. Nature and scope of the present investigation is included at the end of the chapter.

**Chapter-2** discusses about the experimental method and theoretical considerations. In this chapter, the methods of purification of selected solvents for the measurements of density, viscosity and ultrasonic velocity are explained. The instruments and apparatus used for the experimental measurement and their calibrations, adjustments are also presented in this chapter. The comparison of experimental values with literature values and the physical and chemical properties of solvents used in this work are given.

**In chapter-3**, it is aimed to study the intermolecular interactions between the component molecules of the following three binary mixtures:

1. Diethyl malonate + 1-Butanol (BUT)
2. Diethyl malonate + 1-Pentanol (PENT)
3. Diethyl malonate + 1-Hexanol (HEX)

In this chapter, the measured velocities, densities and viscosities along with evaluated thermodynamic and acoustic properties such as molar volume, adiabatic compressibility, intermolecular free length, acoustic impedance, cohesive energy (V, $\beta_{ad,}$ $L_{f,}$ Z, H) are reported at experimental temperatures. The excess properties such as excess molar volume, deviation in adiabatic compressibility, deviation in viscosity, excess intermolecular free length, excess acoustic impedance, excess cohesive energy, excess ultrasonic velocity and Gibb's free energy of activation of flow ($V^E$, $\Delta\beta_{ad,}$ $\Delta\eta$, $L_f{}^E$, $Z^E$, $H^E$, $G^E$) along mole fractions of diethyl malonate at different experimental temperatures are reported. All the parameters are fitted to Redlich-Kister type polynomial equation. The change in velocity, density and viscosity values are linear or almost linear at all temperatures for all systems. The change in values of all excess parameters are non linear and parabolic.

It is observed that excess molar volumes ($V^E$), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess intermolecular free length ($L_f^E$) are observed in negative indicating strong molecular interactions between the components. Deviation in viscosity ($\Delta\eta$), excess acoustic impedance ($Z^E$), excess cohesive energy ($H^E$), excess Gibbs free energy ($G^E$), excess ultrasonic velocity ($U^E$) are observed in

positive trends. This indicates the presence of strong inter molecular interactions between the unlike molecules.

The dissociation of hydrogen bonding between alkanol molecules by unlike molecules and association with diethyl malonate molecules through polarized carbonyl bond (>C=O…..H-O) leading to a contraction in volume of the mixture, which results in negative deviation. It is assumed that $V^E$ values may be affected by the structural characteristics of the components, arising from geometrical fitting of one component into the other's structure, due to the differences in shape and size of components. The specific interactions between unlike molecules of diethyl malonate and 1-alkanols are further confirmed by the positive trends observed for excess acoustic impedance ($Z^E$), excess ultrasonic velocity ($U^E$). As the intermolecular free length decreases sound wave travels short distance which gives positive deviation in excess ultrasonic velocity ($U^E$). As the 1- alcohols are self associated molecules, they form hydrogen bonding with the C=O of the diethyl malonate. The long chain alkanols would increase the basicity of the oxygen and make the hydroxyl proton less available for H- bonding. In addition to this, the consequences of steric hindrance also effects, as the carbon chain length increases, the strength of interaction decreases. Hence, system-1 follows the order

**DEM + BUT > DEM + PENT > DEM + HEX**

***A part of work in these binary liquid mixtures was published in Physical chemistry An Indian Journal.*,11 (2016) 6.**

**Chapter-4** deals with the experimental and various evaluated acoustic and thermo physical parameters for the following mixtures.

1. Diethyl malonate + 2-Methoxy ethanol (MOE)
2. Diethyl malonate + 2-Ethoxy ethanol (EOE)
3. Diethyl malonate + 2-Butoxy ethanol (BOE)

In this chapter, the measured values of velocities, densities and viscosities along with

evaluated excess thermodynamic and acoustic properties at four experimental temperatures were reported.

All the parameters are fitted to Redlich- Kister type polynomial equation. Excess molar volumes ($V^E$), deviation in adiabatic compressibility ($\Delta\beta ad$), excess

intermolecular free length ($L_f^{E)}$, deviation in viscosity ($\Delta\eta$) are observed in negative trends. excess acoustic impedance ($Z^E$), excess cohesive energy ($H^E$), excess Gibbs free energy ($G^E$), excess ultrasonic velocity ($U^E$) are observed in positive trends.

The presence of ethereal oxygen and oxygen present in hydroxyl group of alkoxyalkanols facilitates the formation of intra molecular hydrogen bonding with in the compounds and inter molecular hydrogen bonding with polar carbonyl group of diethy malonate molecules. Hence there may be some inter molecular hydrogen bonding between DEM and alkoxyethanol molecules so that negative $V^E$ values are observed.

The C=O group of ester interacts with -OH group of alkanols through hydrogen bonding. (C=O….OH). On mixing DEM to alkoxyethanols, the dissociation of H-bonds present in the pure alkoxyethanols take place with simultaneous formation of new H-bonds between alkoxyethanol and DEM molecules (between C=O- group of DEM and OH group of alkoxyethanol) leading to contraction in volume. With increase in temperature, break down of hydrogen bonding between self-associated molecules and formation of new hydrogen bonds between DEM and alkoxyethanol molecules takes place, which leads to more contraction in volume and more negative values for $V^E$.

It is observed that the negative excess molar volume decreases with increase in chain length of the alkoxyethanols, indicating the decrease in strength of the hydrogen bonding between the component molecules. This may be due to increased +I effect of the alkyl group, thereby decreasing the polarities of the –OH bond in the alkoxyethanol molecule. The positive values of $G^E$ and $H^E$ suggest the presence of specific and strong interactions like complex formation, strong dipole-dipole interactions etc., between the components of the mixtures. The strength of interactions follows the order

**DEM + MOE > DEM + EOE > DEM + BOE**

***A part of work in these binary liquid mixtures was published in Der Pharma Chemica.,* 8 (2016) 209.**

**In chapter-5**, the selected systems for thermodynamic and acoustic study are

1. Diethyl malonate + Foramide (FA)
2. Diethylmalonate + N,N-dimethylforamide (DMF)
3. Diethyl malonate + N,N-dimethylacetamide (DMA)

In this chapter, the measured values and computed values of molar volume (V), adiabatic compressibility ($\beta_{ad}$), intermolecular free length ($L_f$), acoustic impedance (Z), Cohesive energy (H) and their excess values are tabulated in different tables. All the parameters are fitted to Redlich-Kister polynomial type equation.

The excess molar volumes are negative for the three systems at all the experimental temperatures (303.15, 308.15, 313.15, and 318.15 K). This is occurred by the interaction through >C=O of diethyl malonate and $NH_2$ group of amide molecules leading to contraction of volume resulting in the negative values of $V^E$ indicating the strong interaction.

In the above systems, DEM+FA exhibit stronger interaction than the rest because the hydrogen bonding and dipole–dipole interactions are predominant. As a result of large differences in the size of component molecules, the molecules are readily fitted into the interstitial accommodations of the DEM molecules. In DEM+FA system, the mixing of DEM may induce mutual dissociation of hydrogen bond structures present in pure liquids with subsequent formation of new hydrogen bonds between the proton acceptor of the oxygen atom (with two lone pairs of electrons) of C=O group of the DEM and NH group of the formamide (C=O…..H-N) which would result in the volume contraction resulting in the negative $V^E$ values for DEM+FA mixtures. There is a very large difference between the molar volumes of the two component molecules, which might allow the fitting of the large molecules into each other's structure.

N,N-dimethylformamide (DMF), as a polar solvent, is certainly to some extent associated by dipole-dipole interactions, and is particular interest because of the absence of any significant structural effects due to the lack of hydrogen bonding. DMF is an aprotic solvent with a large dipole moment and high dielectric constant of $\mu = 3.24$ D and $\varepsilon = 36.71$.

Due to the polar nature of the DMF and ester, there exists dipole - dipole interactions in these mixtures. The lone pair of electron present on the N atom of DMF enhances the dipole moment of the C=O group of DEM molecule, which leads to strong interaction among the components of binary mixtures.

Because of the bulkiness of methyl groups in the DMA molecule, the interaction in DMA is less than that of DMF. This is because of the presence of more bulky groups in amide molecule in the former mixtures than that in the later one,

which causes steric repulsion of appreciable magnitude between the component molecules. Steric factor plays a significant role in case of N,N-dimethylforamide and N,N-dimethylaceetamiide. It is observed by the variation in excess inter molecular free length and excess cohesive energy of the system. Deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and excess free length ($L_f^E$) are found to be negative over the entire mole fraction of DEM indicating the presence of strong interaction between the molecules. Positive excess velocity indicates the presence of dipole- induced dipole interaction among the components of binary mixture. The acoustic impedance increases with increase of concentration of diethyl malonate.

The strength of interactions between diethyl malonate and amides is in the order of

**DEM + FA > DEM + DMF > DEM + DMA**

**Chapter-6 is** devoted to study the molecular interactions in the binary mixture of DEM with benzene/mono substituted benzenes over the entire composition range of DEM at temperatures (301.15to 318.15) K. The binary systems investigated are:

1. Diethyl malonate + Nitro benzene (NB)
2. Diethyl malonate + Toluene (TOL)
3. Diethyl malonate + Benzene (BEN)

The non linear variation of ultrasonic velocity, density and viscosity with mole fraction of DEM in all the three systems indicates the occurrence of interactions between the components of liquid systems. Any non-zero value in the excess parameter is a measure of non-linearity and is the confirmation for the existence of interaction among the components of systems. The existence of interactions in liquid mixture is well reflected in excess/deviation properties.

For the system-1 i.e. (DEM + NB) excess molar volume ($V^E$) is negative, where as for the other two systems, (DEM + TOL and DEM + BEN) the ($V^E$) values are in positive trends. For all the three systems deviation in adiabatic compressibility ($\Delta\beta ad$), excess intermolecular free length ($L_f^E$) is negative and deviation in viscosity ($\Delta\eta$) are positive at all temperatures and at all mixed compositions. The parameters excess acoustic impedance ($Z^E$), excess ultrasonic velocity ($U^E$) is positive for all the three systems. Excess cohesive energy ($H^E$) is positive at all compositions and at all temperatures. Excess Gibbs free energy ($G^E$) is positive for all the systems.

A plausible qualitative interpretation of molecular interactions existing in liquid components in studied binaries has been analyzed. The excess molar volume is negative for DEM+ NB and positive for DEM + TOL and DEM + BEN. Nitro benzene is electron attracting group with –I effect so it attract the π electrons thus the volume contraction occurs. As a result negative deviations are observed. The observed $V^E$ are positive for DEM +Toluene. This is due to the fact that the introduction of methyl group ($CH_3$) into the benzene ring, in toluene, being an electron releasing group would enhance the electron density and its donor capacity. Hence toluene would interact more strongly than benzene. The deviations caused by $CH_3$ bond in toluene, which makes weak donor acceptor bond in the mixture with DEM causing positive $V^E$ values. Consequently addition of DEM, a structure breaker causes the maximum destruction of structure of benzene which seems to dominate the effect due to unfavorable packing of plate like benzenes into the spaces created by globular shaped DEM molecules (structural effect). The deviations are in the order of:

**DEM + NB > DEM + TOL > DEM + BEN**.

**Chapter-7** provides information about the theoretical velocities and theoretical viscosities in relation to non-ideal behavior of twelve binary liquid mixtures. A comparison of ultrasonic velocity evaluated from Nomoto's relation, Impedance relation, Van Dael & Vangeel ideal mixing relation, Junjie's relation and Rao's relation with the experimental values has been made for all the twelve binary liquid mixtures. From the values of experimental and theoretically evaluated ultrasonic velocity, it may be concluded that, different theories support different systems based on structures and size of the molecules. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of molecular interactions in the systems studied.

The theoretical viscosities calculated using various theories such as Grunberg-Nissan, Katti-Chaudary, Heric-Brewer, Hind *et al.* and Mc Allister. From the results it is observed that McAllister four body model is best suited for all the systems. With increasing number of interaction parameters, predicting ability of these correlating relations increases.

**Chapter-8** gives the information of partial molar volumes, apparent molar volumes and reduced molar volumes and excess partial molar volumes at infinite dilutions of studied systems. Excess partial molar volumes are negative for all

systems. From this it can be concluded that strong interaction exist in all studied the systems.

**Chapter-9** discusses about the FT-IR spectroscopic studies to give evidence for the existence of hydrogen bonding, dipole-dipole interactions and dipole-induced dipole interactions among the binary liquid mixtures of DEM + 1-alkanols, DEM + alkoxyethanols, DEM + amides. The FT-IR spectra provide a strong evidence for the existence of the strong interactions.

The experimental and calculated data with graphs for binary systems at different temperatures have been given in various tables at appropriate places. The references cited in the body of the thesis are given at the end of each chapter.

Thus, present study on **"*Evaluiation of molecular interactions in certain binaries of diethyl malonate through thermo physical and spectroscopic properties at different temperatures*"** provides a broad understanding of molecular interactions in binary mixtures studied.