Preface

The study of properties of liquid mixtures and solutions finds direct applications in chemical, biochemical, medicine industry and defence. Nowadays ultrasonic technique is the powerful tool in providing information regarding the molecular behavior of liquids owing to its ability of characterizing physiochemical behavior of the medium. Many engineering problems require qualitative data on the ultrasonic velocity and density of liquid mixtures hence it has been a subject of active interest during the recent years. Derived parameters from ultrasonic speed measurement and the corresponding excess functions provide qualitative information regarding the nature and strength of interactions in liquid mixtures/solutions. In view of the above importance of liquid mixtures/solutions in various industries, I have chosen such studies both in aqueous and non-aqueous solutions and liquid mixtures for my research work. The thesis is divided in to seven chapters

Chapter 1 gives an introduction about some theories of liquids/liquid mixtures and structures of water. The review of research work is mainly focused on ultrasonic, volumetric and viscometric studies of molecular interactions in aqueous – electrolytes, aqueous – non electrolytes and non aqueous – non electrolytes liquid solutions/mixtures is also presented in this chapter.

Chapter 2 emphasizes the various experimental techniques employed in the present investigation. Ultrasonic interferometer method for the measurement of ultrasonic velocity, doubled-walled pyknometer for the measurement of density and Ostwald viscometer method for measurement of viscosity have been employed in the present study.
Chapter 3 narrates the various equations employed to compute the acoustic, thermodynamic and transport properties of liquid mixtures/systems. Deviation/excess acoustic, volumetric and viscometric properties have also been discussed in this chapter to study the molecular interactions in the present investigated mixtures/solutions. Partial molar properties of liquid mixtures are also discussed in this chapter. Various theoretical models and polynomials for measuring the ultrasonic velocity and viscosity have been discussed in this chapter.

Chapter 4 reports the ultrasonic and volumetric study of molecular interactions in some binary and equimolar liquid mixtures at 308.15 K. This chapter has been divided into two sections. In section-A, molecular interactions in the binary mixtures of N,N-dimethyl formamide (DMF) with methyl acrylate (MA) or ethyl acrylate (EA) or butyl acrylate (BA) or 2-ethyl hexyl acrylate (EHA) have been presented. In section-B of this chapter molecular interactions in the mixtures of 1-butanol/iso-butanol/t-butanol with equimolar mixture of N,N-dimethyl acetamide (DMA) and ethyl acrylate (EA) have been reported. Ultrasonic velocity and density have been determined over the entire range of composition of various butanol used. From the experimental results of ultrasonic velocity and density the properties such as deviation in ultrasonic velocity, \((\Delta u)\), deviation in isentropic compressibility, \((\Delta k_s)\), excess molar volume, \((V_m^E)\), excess inter molecular free length, \((L_f^E)\) and excess acoustic impedance, \((Z^E)\) have been calculated. The variation of these properties with composition of the mixtures has been discussed in terms of molecular interactions in the present investigated mixtures.

The excess/deviation properties have been fitted to Redlich-Kister type polynomial equation and also the corresponding standard deviations have been computed. Besides, the
experimental values of ultrasonic velocity for all the investigated liquid mixtures have been measured and compared with the theoretically estimated values using different empirical relations such as, Nomoto’s, Van Dael and Vangeels ideal mixing relation, Impedance dependence relation, Junjie’s relation, Jacobson’s equations and Rao’s specific sound velocity. The percentage deviations of theoretical velocities from experimental values are also calculated. Theoretical ultrasonic velocity data is used to study molecular interactions in the binary systems investigated. Further, the experimental data have been fitted to two special types of polynomial equations which describe the ultrasonic velocity data quantitatively as well as qualitatively even in the specific interaction predominant region where non-ideal behavior of the system is noticed.

In section A, The $V_{m}^{E}$, $\Delta k_{s}$ and $L_{f}^{E}$ values are positive whereas $\Delta u$ and $Z^{E}$ values are negative in all the binary mixtures, indicating dispersion forces between the acrylate and DMF molecules follow the order MA+DMF>EA+DMF>BA+DMF>EHA>DMF. The partial molar volumes, $\overline{V}_{m,1}$, $\overline{V}_{m,2}$, and excess partial molar volumes, $\overline{V}_{m,1}^{E}$, $\overline{V}_{m,2}^{E}$ are also calculated. The observed higher partial molar volumes in the liquid mixture when compared to the respective molar volumes of pure components indicating weak interactions present in the systems. In section B, negative values of $V_{m}^{E}$, $\Delta k_{s}$, $L_{f}^{E}$ and positive values of $\Delta u$, $Z^{E}$ have been observed over the entire composition range. The observed negative and positive values of deviation/excess properties are attributed to the strong interactions between the unlike molecules of the mixtures. The strength of interaction in the mixtures follow the order (DMA+EA) +, t-butanol > iso-butanol > 1-butanol.
[The work reported in the section-A of this chapter is published in Journal of Chemical Thermodynamics, 43 (2011) 1844-1850 (Elsevier Publishers) and the work presented in section-B is published in Journal of Thermodynamics, Volume 2014, Article ID 124012 (Hindawi Publishers)

Chapter 5 gives volumetric and viscometric study of some liquid mixtures has been presented at various temperatures like 303.15 K, 313.15 K and 323.15 K. This chapter is divided into two sections namely, Section-A and Section-B.

Binary mixtures of Propanoic acid (PA) with N,N-Dimethyl aniline (DMA) and N,N-Diethyl aniline (DEA) are presented in section-A. Propanoic acid (PA) with equimolar mixture of N,N-dimethyl formamide (DMF) + methanol (MOH)/ethanol (EOH)/1-propanol (POH) are depicted in section-B. In this chapter we reported densities (ρ) viscosities (η) of the liquid mixtures and the deviation/excess properties such as deviation in viscosity, (Δη), excess Gibb’s free energy of activation of viscous flow, (ΔG*E), excess molar volume (VmE), partial molar volumes, (Vm1, Vm2), excess partial molar volumes, (Vm1E, Vm2E), partial molar volumes at infinite dilution, (Vm1∞, Vm2∞) and excess partial molar volumes at infinite dilution (Vm1E∞, Vm2E∞). The variations of these properties with composition as well as with temperature have been discussed in terms of molecular interactions existing among the molecules of these mixtures. Deviation/excess properties have been fitted to Redlich-Kister type polynomial equation. The experimental viscosity data of all liquid mixtures are correlated to the viscosity models such as Grunberg and Nissan, Hind et al., Katti and Chaudhrai, and Heric and Brewer.]
In section-A, the results indicate the presence of strong specific interactions such as interactions between proton of propanoic acid and lone pair of electrons on the nitrogen atom of aniline and due to the observed difference in molar volumes of propanoic acid and substituted aniline is responsible for the observed negative $V_m^E$ and positive $\Delta \eta$ values in the present investigated systems. The strength of interactions follows the order N,N-diethyl aniline + propanoic acid > N,N-dimethyl aniline + propanoic acid. The strength of interactions is also studied with the variation of temperature.

The values of $V_m^E$ are negative and $\Delta \eta$, $\Delta G^{\text{vE}}$ are positive at all temperatures studied in section-B, indicating the presence of strong interactions (hydrogen bonding O…..H-O-) such as interactions between carbonyl group(-C=O) of amide molecules and hydroxyl group(-OH) of alcohol groups and also the intermolecular interactions between carbonyl group(-C=O) of acid molecules and hydroxyl group(-OH) of alcohols, dipole-dipole interactions and geometrical fitting of smaller molecules into the voids created by the larger molecules in the investigated systems. The strength of interactions follows the order (DMF+MOH) +PA < (DMF+EOH) +PA < (DMF+POH) +PA. The calculated values of partial molar volumes and excess partial molar volumes at infinite dilution have also been indicating the existence of strong interactions among the unlike molecules in the mixtures. The experimental viscosity values are compared with the viscosity values obtained from different empirical relations and these are in good agreement with the experimental values.

[The work reported in section – A is published in Journal of Chemical Engineering Data, 57 (2012) 352 (ACS publications) and the work related to section – B is published in Journal of Solution Chemistry, 42 (2013) 494 (Springer Publications)
Chapter 6 briefs the molecular interactions in aqueous-electrolyte and aqueous-non-electrolytic solutions have been discussed and this chapter is divided in two sections. In section A, ultrasonic, volumetric and viscometric study of aqueous-electrolyte solutions is explained. 0.1 (m) molality of aqueous tripotassium citrate and 0.1 (m) molality of aqueous trisodium citrate (electrolytes) solutions in methanol are prepared. Ultrasonic and thermodynamic study of aqueous non-electrolyte solutions of 0.5 m, 1.0 m and 1.5 m (molality) ethylene glycol/propylene glycol in iso-propanol are discussed in section-B. From the experimental results of ultrasonic velocity, \(u\), density, \(\rho\) and viscosity, \(\eta\) properties of relaxation time, \(\tau\), relative association, \(RA\), relaxation strength, \(\alpha\) and deviation/excess properties such as deviation in ultrasonic velocity, \(\Delta u\), deviation in isentropic compressibility, \(\Delta k_s\), excess molar volume, \(V_m^E\), excess inter molecular free length, \(L_f^E\), excess acoustic impedance, \(Z^E\), deviation in viscosity, \(\Delta \eta\), excess free volume, \(V_f^E\), excess internal pressure, \(\pi^E\), excess enthalpy, \(H^E\), excess relaxation time, \(\tau^E\), excess Gibb’s free energy of activation of viscous flow, \(\Delta G^E\) have been also computed and these properties have been discussed in terms of molecular interactions in the present investigated solutions. The deviation/excess properties have been fitted to R-K type polynomial and the corresponding standard deviation are also calculated.

The measured values of ultrasonic velocity for all the investigated solutions compared with the theoretically estimated values using different empirical relations such as, Nomoto, Van Dael and Vangeels ideal mixing relation and Impedance dependence relation. The percentage deviations of theoretical velocities from experimental values are also evaluated. The experimental viscosity data of all liquid solutions are correlated to the viscosity models such as Grunberg and Nissan, Hind et al., Frenkel. In section-A, positive
and negative deviation/excess properties are attributed to strong specific interactions such as formation hydrogen bond, dipole-dipole interactions and geometrical fitting of smaller entities in to larger entities. The strength of interaction is predominant in case of propylene glycol compared to ethylene glycol in iso-propanol solution. On comparison of molalities, interaction is more in 0.5 m aqueous glycol with iso-propanol compared other two molalities in section-B.

Chapter 7 reported the ultrasonic, volumetric and viscometric study of molecular interactions in some non aqueous – non electrolyte liquid mixtures at 308.15 K. For the sake of convenience this chapter is divided into two sections namely, section-A and section-B. Binary mixtures of Dichloromethane (DM) and 1,2-Dichloroethane (DE) with N,N-dimethyl formamide (DMF) and Dimethyl sulfoxide (DMSO) are presented in section-A. In section-B binary mixtures of Ethylene glycol (EG) with formamide (FA), N,N-dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA) have been investigated. In section-A, from the experimental data of ultrasonic velocities, (u), densities, (ρ) and viscosities, (η), deviation properties like deviations in ultrasonic velocity, (Δu), isentropic compressibility, (Δk_s), isothermal compressibility, (Δβ_T), thermal expansion coefficient, (Δα) and excess properties like excess intermolecular free length, (L_f^E) and excess acoustic impedance, (Z^E), deviation in viscosity, (Δη), excess free volume, (V_f^E), excess internal pressure, (π_i^E), excess enthalpy, (H_i^E), excess relaxation time, (τ_E), excess Gibbs free energy, (ΔG_i^E) have been measured. The deviation/excess properties have been fitted to Redlich-Kister type polynomial and the corresponding standard deviations have been calculated. From the positive and negative values of excess properties strong interactions such as hydrogen bond
formation between the dissimilar molecules, dipole-dipole interactions and interstitial accommodation of unlike molecules are favourable factors for the responsible properties.

The $\overline{V}_{m,1}$, $\overline{V}_{m,2}$, $V^E_{m,1}$, and $\overline{V}^E_{m,2}$ have been computed from the experimental results. The calculated values of partial molar volumes and excess partial molar volumes at infinite dilution data supports the conclusions drawn from $V^E_m$. The $\overline{K}_{m,1}$, $\overline{K}_{m,2}$, $\overline{K}^E_{m,1}$, and $\overline{K}^E_{m,2}$ have been computed from the experimental results. The experimental ultrasonic velocity data of all binary liquid mixtures are correlated to the Nomoto, Vandael and Impedance relations. The viscosity models such as Grunberg and Nissan, Hind et al., and Frenkel.

In section-B, from this experimental data, excess molar volume, $(V^E_m)$, deviation in viscosity, $(\Delta\eta)$, and excess Gibbs free energy of activation of viscous flow, $(\Delta G^*E)$ have been determined. These deviation/excess properties have been fitted to Redlich–Kister type polynomial. These observed properties are negative values, which are due to the addition of amide molecules causes breaking of the hydrogen bonds between EG molecules and the subsequent formation of strong hydrogen bonds between the hydrogen atom of –OH group of glycol molecules and oxygen molecule of >C=O group of amide molecules and fitting of smaller molecules into the voids created by the bigger molecules and also due to the dipole-dipole interactions between the unlike molecules causes the strong specific interactions exist between the unlike molecules.

[The excess molar volumes and partial molar volumes data reported in section – A is published in International Journal of Research in Pure and Applied Physics, 3(4) 2013 43-49 and the ultrasonic data in section – A is published in Journal of Molecular Liquids, 195 (2014) 110-115 (Elsevier Publications)]