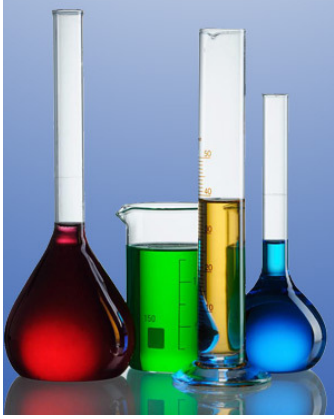
Chapter 6

SUMMARY



CHAPTER 6

SUMMARY

The studies of thermo dynamical and transport properties of binary liquid mixtures and solutions have found wide applications in chemical, textile, leather and many other industries.

For a better understanding of the physico- chemical properties and the molecular interactions between the participating components of these mixtures, ultrasonic velocities together with density and viscosity are measured at different temperatures for different concentrations of the components in the mixture. These data furnish wealth of information about the interactions between ions, dipoles; hydrogen bonding, multi polar and dispersive forces. In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than the actual values.

The mixing of different components gives rise to solutions that generally do not behave ideally. The deviation from ideality is expressed by many thermodynamic variables, particularly by excess or residual extensive properties. Excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property if they behave ideally, and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute- solute, solvent - solvent and solvent - solvent species.

The present thesis deals with the studies on densities, viscosities, speed of sound velocities and excess viscosity (η^E), excess molar volume (V^E), excess Gibbs free energy of activation of viscous flow (G^{*E}), excess acoustical parameters such as excess ultrasonic velocity (u^E), excess isentropic compressibility (K_S^E), excess intermolecular free length (L_f^E) and excess acoustic impedance (Z^E) have been determined for binary mixtures of carbitols and different amines at 308.15 K over the whole range of composition. The carbitols are methyl carbitol, ethyl carbitol and butyl carbitol as non-common components and n- butyl amine, sec - butyl amine, ter- butyl amine, n- hexyl amine, n- octyl amine and cyclohexyl amine as common components. The results are

incorporated in the form of thesis and are divided into six chapters and each chapter is further divided into several sections.

Chapter 1 deals with the general introduction on molecular interactions present in binary mixtures on the basis of solute- solute, solute-solvent and solvent-solvent interactions. The theories relating to studies of molecular interactions in the binary mixtures are also included in this chapter.

Chapter 2 presents a brief survey of literature pertaining to the present studies on the measurement and use of viscosities and ultrasonic velocities of binary mixtures to understand the nature of molecular interactions respectively. It is also gives the aim and scope of the present investigations.

Chapter 3 deals with the materials and experimental methods. This gives the purification of liquids used in the present study along with the various methods for the determination of densities and viscosities in brief and the methods employed in the present study in detail.

The pycnometer method used for measuring the density gave results with an accuracy of one in 10^4 parts. This chapter also explains the viscosity measurements using Ubbelohde suspended level viscometer (10-15 cm^3). The reported viscosity data are reproducible with in ± 0.1%. This chapter also describes the measurement of the ultrasonic velocities which were measured with a single crystal interferometer at a frequency of 2MHz and these were accurate to ± 0.15 %. Temperature was maintained at 308.15 K by circulating water from a constant temperature bath which was controlled with in ± 0.05 K.

Chapter 4 deals with the volumetric and viscometric studies and is divided into 4 Sections. Section-1 gives the brief introduction on the viscosity and molar volume studies to understand the intermolecular interactions in binary liquid mixtures. This section also gives the various equations used to calculate the other parameters using experimentally measured density and viscosity data. Sections-2, 3 and 4 discusses the results obtained relating to the viscosity and molar volume studies of binary liquid mixtures of amines with Methyl carbitol (MC), Ethyl carbitol (EC) and Butyl carbitol (BC) at 308.15 K respectively. The excess properties like excess viscosity (η^E), excess molar volume (V^E),

excess Gibbs free energy of activation of viscous follow (G^{*E}) and Grungberg – Nissan interaction parameter (d^1) are evaluated from the measured density and viscosity.

Excess property data ($V^{E,}$ η^E and G^{*E}) are interpreted in terms of two factors (i) breakup of the hydrogen bonds in associated aggregates of amines and non - common components and (ii) interstitial accommodation of one component into another component and the possible hydrogen bonding interactions. The positive values of V^E and the negative values of η^E and G^{*E} for the present binary liquid mixtures suggest the dissociation of component liquids through break-up of hydrogen bonds whereas the negative values of V^E and positive values of η^E and G^{*E} have been attributed to the presence of the specific interactions (such as hydrogen bonding etc.) between amines and non - common components. The positive d^1 values attribute to the presence of strong interactions in the binary systems. From the viscosity and molar volume studies of these binary mixtures it is concluded that the molecular interactions are in the following order in case of amines + carbitols

MC or EC or BC + NOA > + NHA > +CHA > +TBA > +SBA > +NBA

This order in the case of amines under study may be ascribed to the effect of the increase in the chain length and the strength of specific interactions which lead to the complex formation between unlike molecules. The same explanations holds good in case of branched amines, where the interactions increased in non common component + branched amines as the amines becomes more and more branched. The result further confirmed the presence of more interactions in CHA + non common component when compared to NHA + non common component mixtures.

Chapter-5 discusses the ultrasonic velocity studies for the binary liquid mixtures under study and is again divided into 4 Sections. Section-1 explains how the ultrasonic velocity study is useful as a powerful tool for investigating the departure of liquid mixtures from ideality. This section also gives the details about the various equations used to calculate the different acoustical parameters from the measured densities (ρ) and ultrasonic velocities (u). The parameters calculated are acoustic impedance (z), isentropic compressibility (k_S), intermolecular free-length (L_f), relative association (R_A) and excess functions like excess isentropic compressibility (k_S^E), excess intermolecular free-length (L_f^E), excess ultrasonic velocity (u^E) and excess acoustic impedance (Z^E)

which are used to discuss the molecular interactions in the binary systems. The Sections 2 to 4 explains the results obtained in the study of ultrasonic velocity of binary liquid mixtures of different carbitols (non-common components) with different amines.

The variations of u, K_S, L_f and R_A with the mole fraction of solvent of these binary mixtures indicate the presence of specific interactions between the unlike molecules. The above results are further discussed by studying the variations in excess acoustical properties such as K_S^E, L_f^E, Z^E and u^E with the mole fraction of the solvent. The negative K_S^E and L_f^E and the positive Z^E and u^E values are attributed to the presence of strong specific interactions whereas positive K_S^E and L_f^E and negative u^E and Z^E values are attributed to the weak interactions.

The order of interactions from negative values of K_S^E, L_f^E and positive values of u^E and Z^E for present carbitols and amines are shown below

MC or EC or BC < + CHA < + NHA < +NBA < + SBA < + TBA

These are in accordance with the volumetric & Viscometric results of these systems.

Chapter 6 summarizes the results obtain in the systems studied.