SUMMARY

The thesis entitled "Applications of viscosity, density and ultrasonic measurements in organic binary mixture" consists of the measurements of the densities, viscosities and ultrasonic velocities of binary liquid mixtures. Mixing properties of various liquid mixtures have been investigated by many workers in order to have insight into the type and extent of intramolecular and intermolecular interactions. Accurate knowledge of thermodynamic mixing properties of such binary mixtures has great relevance in theoretical and applied areas of research. These data are needed for design processes in chemical, petrochemical and pharmaceutical industries. Usually for nonideal mixtures direct experimental measu--rements are performed over the entire range of composi--tion. Many times predictive methods for the excess quantities would be more useful than the direct experimental measurements, especially when quick estima--tes are needed. Most empirical approaches for calcula--ting the excess properties, an attempt to explain solution nonidealities in terms of specific or nonspecific intermolecular interactions. In order to

investigate intermolecular interactions between DMSO and alkanols, $PhNO_2$ and alkanols, DMSO and $PhNO_2$ binary mixtures of these systems have been prepared over entire composition range and their densities, viscosities and ultrasonic velocities at various temperatures have been measured and reported in the present thesis.

The first chapter of the thesis describes the historical development of the subject. An account of the work particularly density, viscosity and ultraso--nic velocity has been taken in detail. The theore--tical methods of evalution of different interaction parameters based on the two body collision theory, such as Grunberg Nissan (d), Choudhri-Katti (W_{vis}), Tamura Kuratta (T_{12}) and Hind (H_{12}) are described. Interaction parameters such as ν_{12} and ν_{21} of McAllister equation and δ_{12} of Heric equation have been discussed. The method of evaluation of viscosity of ternary mixture is also explained with the help of Erying equation. Theoretical equations have been discussed in this chapter to calculate excess volumes of binary and ternary liquid mixtures. An account has been also taken of theoretical evaluation of ultrasonic

velocity through the liquid mixtures based on Schaff's collision factor theory, free length theory, Van dael and Van geel, and Nomoto equations.

The detailed descriptions of experimental techni--ques used in present investigation have been included in second chapter. The density, viscosity and ultra--sonic velocity are measured with the help of bicapilla-ry pycnometer, Ostwald viscometer and ultrasoni interferometer respectively. All these measurements are made in thermostated waterbath having thermal stability of $\pm$ 0.01 ^{0}C. The accuracies in these measu--rements are $\pm$ 0.0001 gm/ml, $\pm$ 0.003 cP and $\pm$ 0.03 % respectively.

In third chapter viscosity, studies of binary liquid mixtures of DMSO-alkanols, $PhNO_2$-alkanols, DMSO-$PhNO_2$ and ternary liquid mixtures of DMSO-$PhNO_2$-MeOH have been presented. Viscosity measurements are made at the temperatures ranging between 25-40 ^{0}C. All the efflux times of constant volume of liquid are measured with the help of stop watch accurate to $\pm$ 0.01 sec. All the efflux times are greater than 100 seconds and hence kinetic energy correction to viscosity measureme--nts is not necessary. From these viscosity measureme--nts change in viscosities ($\Delta\eta$) interaction parameters

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mainly Grunberg Nissan (d), Choudhri Katti (W_{vis}), Tamura Kuratta(T_{12}) and Hind (H_{12}), V_{12}, V_{21} and δ have been computed. The excess free energy of activation of flow (ΔG^{*E}) has been also calculated for these binary mixtures. Viscosity deviation ($\Delta\eta$) values for DMSO-alkanol are negative and increase with increase in temperature. Therefore the existence of dispersive forces between DMSO and alkanol molecules are concluded. It is further concluded that breaking of associated molecules of alkanol dominate over the weak Hydrogen bonding between DMSO and alkanol. The resulting viscosity of DMSO-alkanol mixture is explai--ned on (1) depolymerisation of associated agreegates to monomeric moities and (2) to the contact between unlike molecules. The presence of dispersive forces between these have been corroborated from low and negative magnitudes of interaction parameters. This observation is in accordance with that of Mahl and Nigan. The other interaction parameters such as W_{vis} , T_{12}, H_{12} are either positive with very small magnitudes or negative with high magnitudes, suggesting the absence of specific interaction. The dispersion between DMSO and alkanol molecules is further supported by the

positive values of $\Delta^{*}G^{E}$. Similar observations as regards $\Delta\eta$, W_{vis} , H_{12} , T_{12}, $\Delta^{*}G^{E}$ for $PhNO_2$-alkanol mixtures are made, suggesting also the presence of dispersive forces in $PhNO_2$-alkanol mixtures. In the system DMSO-$PhNO_2$ positive $\Delta\eta$ and positive d values suggest the presence of specific interactions, however according to Fort and Moore the presence of specific interaction forces in mixtures of DMSO-$PhNO_2$ can be considered as unrealistic, since simple magni--tudes and sign of $\Delta\eta$, d do not predict correctly the type and strength of interactions when molecular sizes of two components differ considerably. In the case of DMSO-$PhNO_2$, molecular sizes of two constituents of the mixture differ considerably and hence the criterion of positive $\Delta\eta$ and d for the presence of specific interactions between DMSO and $PhNO_2$ molecules can not be taken as Valid. $\Delta^{*}G^{E}$ values of this mixture also suggest the absence of specific interactions between DMSO and $PhNO_2$ molecules. Deviation in viscosity ($\Delta\eta$) of ternary liquid mixtures under investigation is negative.

In order to have a realistic insight into the

intermolecular interactions in these binary mixtures, the excess molar volumes (V^E) and contact interaction parameter (A_{12}) of these binaries have been calculated from their density values. Excess molar volume (V^E) values of DMSO-alkanols are mostly negative while those for DMSO-isoalcohols are slightly negative or positive, suggesting specific interactions between DMSO-and-n-alkanols and nonspecific interactions between DMSO and isoalkanols. Interaction parameter (A_{12}) is negative for DMSO-alkanol mixtures at all temperatures in low DMSO region. It gradually increases with increase of DMSO and ultimately it becomes positive. V^E values for $PhNO_2$-alkanol systems at all temperatures are negative suggesting presence of strong specific interactions between alkanol and $PhNO_2$ molecules. This is further supported by the negative values of contact interaction parameters (A_{12}). The presence of disper--sive forces between DMSO and $PhNO_2$ molecules is further confirmed from large positive V^E values and positive A_{12} values.

In fourth chapter, ultrasonic velocity measurements through these mixtures at various temperatures are

presented. From the knowledge of ultrasonic velocity and density of the liquid mixtures, different thermo--dynamic properties such as isentropic compresibilities (Ks), inter molecular free length (Lf), specific acoustic impedence (Z), relative association (R_A), molar sound velocity (R), molecular association (M_A) and available volume (Va) have been calculated. Ultrasonic velocities along with these derived parame--ters are excellent tools to detect the intermolecular interactions in liquid mixtures. The excess isentropic compressibilities ($\triangle$ Ks), excess available volume (Va^E), excess specific acoustic impedence (Z^E), excess free length (L_f^E) are better criteria than their absolute values to detect the type of interactions. Hence these excess properties of titled binaries are also evaluated at different temperatures. Ultrasonic velocities of these binary mixtures have been theoretically computed using Nomoto, collision factor theory (CFT), free length theory (FLT) and are compared with experimental values. The variation of ultrasonic velocity with compressibility of liquid mixture is explained on the model for sound propogation proposed by Erying and

Kincaid. This model has been found to be suitable in all binary mixtures. It is further observed that the ultrasonic velocity (U) increases and free length (L_f) decrease with increase $PhNO_2$ and DMSO in the correspo--nding binary mixtures. This suggested strong specific interactions between unlike molecules of binary mixtures. Ultrasonic velocity and intermolecular free length are found to increase with increase of DMSO in DMSO-$PhNO_2$ mixtures indicating the presence of dispersive forces between these molecules. The above inferences are confirmed further from the derived parameters such as isentropic compressibility (Ks), acoustic impedence (Z), Molar sound velocity (R), relative association (R_A), avai lable volume (Va). The criterion of deviation of M_A from unity also supports the above inferences. Deviation in isentropic compressibility, excess free length, excess specific acoustic impedance and excess available volume have been calculated from the equation of the form

$$A^E = A_{exp} - A_1X_1 - A_2X_2$$

Where A stands for particular property and X_1 ,

X_2 are mole fractions of constituents. The negative excess values of all these properties for DMSO-alkanol mixtures and $PhNO_2$-alkanols mixtures suggest the specific interactions between constituent molecules while positive values of these parameters for DMSO-$PhNO_2$ mixtures suggest non specific interaction.