EXCECUTIVE SUMMARY OF THE MINOR RESEARCH PROJECT

Title of the Project: Viscosity of aliphatic & aromatic aldehydes and their binary mixtures with polar and non polar solvents at different temperatures.

Principal Investigator: Dr. Satish B. Maulage, Assistant Professor in Chemistry.

The project work is divided into four parts. Part-I provides information about basic principles involved in viscosity measurement. Part-II reveals all the experimental and mathematical details of binary mixture systems. It describes experimental methodology for the measurement of density and viscosity, determination of viscosity deviations $\boldsymbol{\Delta\eta}$, molar volumes $\mathbf{V_m}$, excess molar volumes $\mathbf{V^E}$ and excess free energies of activation of viscous flow $\mathbf{\Delta G^{*E}}$ of binary liquid systems. Part-III includes the studies of experimental results of binary liquid mixtures of aldehydes with alcohols as a function of composition at 298.15 K, 308.15 K and 318.15 K temperatures and the experimental data is used to determine Viscosity deviations $\Delta\eta$, molar volumes V_m, excess molar volumes V^E and excess free energies of activation of viscous flow ΔG^{*E} of binary liquid mixtures. In part-IV, the conclusions have been drawn from the data obtained experimentally and proposed some recommendations regarding the future scope in this outlined research area.

Viscosity is the property which opposes the relative motion of adjacent portions of the liquid and can consequently be regarded as a type of internal friction. Viscosity is an important physical property which characterizes a simple liquid's resistance to flow. Viscosity is the measure of the internal friction in liquid or a resistance of a flow. For certain liquids viscosity only depends on temperature and pressure. This group of materials is known as Newtonian liquids. Liquids which do not follow this proportional ratio are called non- Newtonian. In practice, viscosity which is time-dependent is called thixotropy. If a liquid is sheared at a

constant velocity gradient, viscosity will be slowly decreased. When the shear forces are removed, viscosity will recover and return to the initial value. The viscosity of pseudo plastic materials will decrease with an increasing shear rate (shear thinning).

The viscosity of pure liquids as well as those of liquid mixtures has attracted the attention of many researchers over past few the years. In spite of all the earlier contributions, complete description of the viscosity of multi-component liquid mixtures remains insufficient. This can be attributed to the difficulty of understanding the structure of the liquids. That is why accurate and reliable viscosity data, especially for liquid mixtures are needed. Beside this viscosities of binary liquid mixtures are required in many industrial and engineering applications involving mass and heat transfer processes. Accuracy in the design or performance of industrial equipment for handling operations or processes involving binary solutions requires accurate physical data on the solutions involved. For engineering utility, reliable solutions over wide range of concentration and temperature would be extremely valuable. Accurate viscosity data are needed for the design of most of liquid flow equipment. The lack of knowledge regarding the structure and the complex nature of liquids and the little knowledge currently we have about the intermolecular forces in liquid systems, this research work can contribute to the current unsatisfactory methods regarding the prediction of physical properties of liquid systems. The Viscosity study of liquids plays an important role to understand the nature and strength of molecular interactions. Viscosity measurements have been properly used in order to explain the nature of molecular interaction in pure liquids and their binary mixtures. Volumetric properties of binary mixtures of aldehydes with alcohols, in conjunction with other thermodynamic properties provide useful information about liquid-liquid interactions. Density and viscosity of binary mixtures are required in both physical chemistry and chemical engineering calculations involving liquid flow, heat and mass transfer. Consequently, reliable and accurate data which can

be applied to wide ranges of temperatures are required. The values of such quantities may sometimes be obtained from tables but it is usually found that even the most extensive tables do not contain all the data necessary for designing a technological process. The properties of fluid mixtures are required to understand the molecular interactions. It is usually found that the properties have only been studied for the pure components from which the liquid mixtures are constituted and some methods are required for estimating the properties of the mixtures from those of pure substances. Such predictions usually entail considerable difficulties. The most difficult case occurs when the properties of the pure liquid or mixture in question have not been measured at all. In this case the only information available may be the structural formula of the given compound. Although values of the necessary quantities can sometimes be estimated, it would clearly be preferable to perform the appropriate measurements and to determine the values of the properties under consideration experimentally.

Densities of liquid mixtures and related volumetric properties such as excess molar volumes are required for theoretical calculations as well as applications. For the practical proposes the knowledge of volume of liquid mixture is important than the corresponding density value. The sign and magnitude of excess molar volume gives good estimate of strength of unlike interactions in binary mixtures. Large positive values for V^E are taken, as indicative of weak interactions whereas, large negative values of V^E are usually found when these interactions are strong and intermolecular association are believed to be present.

The knowledge of viscosities of fluids is required in most engineering calculations where fluid flow, mass transport and heat transport are important factors. Viscosity data gives valuable information about the nature of interaction forces operating within and between molecules. In the recent years the employment of computer simulation methods of molecular dynamics has led to significant progress towards a successful molecular theory of transfer properties in dense fluids

and a greater understanding of molecular motions and interaction patterns in system showing dispersion and specific interaction in non electrolytic liquid mixture involving both non hydrogen bonding and hydrogen bonding solvents. Many attempts have been made to interpret viscosity data theoretically or empirically. A very common approach is to correlate the measured values of excess properties from the pure component properties without any experimental knowledge of the actual system itself.

Viscosity is the characteristic property of a liquid-liquid that mainly characterizes its flow behavior. The concept of viscosity reveals the idea of the internal friction between the molecules of the liquid for, whenever any part of a liquid is caused to move, neighboring parts tend to be carried along also. This resistance to the development of velocity differences within a fluid is the essential feature of viscosity and it forms the basic of the quantitative assessment of viscosity. From the industrial production and fundamental science point of view, the measurement of viscosity is of considerable importance. Viscosity is the quantity that determines the forces to be overcame when liquids are used in pipelines or bearing, and it controls the flow of liquid in such processes. Another application of viscosity measurement affords a convenient means of checking the constancy of a product. Viscosity measurement has also proved to be a valuable tool for the physical chemist since the viscosity coefficient is profoundly influenced by the size, shape and arrangement of the molecules.

The thermodynamic parameters such as density, viscosity, deviation in viscosity, excess molar volumes and excess free energies of activation of viscous flow for the binary mixtures of aldehydes with alcohols over the entire range of compositions and at different experimental temperatures can be under stood by the interaction processes of solvent-solvent depend on the structure, nature of the solvents, mole fraction and these interaction processes occurring by weak forces like van-der-waals forces (dispersion forces) are primary responsible for the interaction

between the compound molecules. The aim of the present investigation was to study the physical properties and to collect new experimental data on various thermodynamic parameters as outlined above. Furthermore, the study involved the evaluation of the excess functions and interaction parameters from the experimental data and interpretation of the intermolecular interactions and testing of various existing theoretical models of viscosity. Therefore in view of these considerations, the study of liquid-liquid binary mixtures involving formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, cinnamaldehyde and anisaldehyde as a primary solvents with Methanol, Ethanol, n- propanol and n-butanol as secondary solvents were considered. In chemical industry, knowledge of the thermodynamic properties of binary mixture solutions is essential in the design involving chemical separation, heat transfer, mass transfer and fluid flow. In the recent years there has been renewed interest in the study physico-chemical properties of drug molecules and its interpretation in terms of solute-solvent interactions. Thus, present work was undertaken considering the importance of thermodynamic properties in understanding solute-solvent, solvenet-solvent interactions. In this regard, combinations of binary liquid mixtures were studied at 298.15 K, 308.15 K and 318.15 K and at atmospheric pressure. The characteristic of present work was that it involves the study of some thermodynamic parameters of liquid-liquid mixtures involving aliphatic and aromatic aldehydes and polar alcohols. The results obtained from the various thermodynamic parameters studied throws some light on the nature of intermolecular interaction between various binary mixtures of aldehydes with alcohols. In case of binary mixtures involving alcohols, the presence of specific interaction as well as structural contributions arising from the geometrical fitting of one component molecule into the other, due to difference in the molar volume and free volumes between the components was observed. The specific interaction was found in case of methanol whereas in case of other alcohols, as chain length increases, size increases and dielectric constant

values decreases, specific interaction decreases and the structural contributions arising from the geometrical fitting found increased. The increase in temperature tends to increase structural interactions because of better interstitial accommodation due to thermal agitations. The dispersion interaction was observed in case of binary mixtures of aromatic aldehydes. This dispersion interaction may arise due to breaking of cohesive forces acting in like molecules. The increase in chain length and temperature found to increase dispersion interactions. The study of thermodynamic properties of binary mixtures of aromatic aldehydes reflected the presence of dispersion interaction as well as structural interactions arising from the geometrical fitting. The results of various properties showed presence of dipole- dipole interactions as well as structural interactions and an increase in dispersion interactions as substitution increased.

This study can be extremely helpful in elucidating the changes occurring in the various liquid binary mixtures. Since the present work involves aliphatic and aromatic aldehydes, the study can be put into use to understand macromolecular interactions and to correlate to its therapeutic effects. This study can be further extended to study ternary liquid mixture systems and their interaction parameters. Moreover, this work can be corroborated with dielectric constant measurements, surface tension measurements, heat capacities from calorimetric measurements, infrared and nuclear magnetic resonance spectroscopy to enhance the further development and to explain the molecular interactions using different models quantitatively which is rather a challenging task.