1. INTRODUCTION

Thermodynamic properties of liquid mixtures are very important as fundamental data in process design and are also helpful to understand characteristics of solutions. The excess volume is one of the fundamental thermodynamic property for which a large number of data have been accumulated in recent years. It has always been desirable to predict the excess volume behaviour of binary system using constituent pure-liquid data only. Similarly, ultrasonic studies have been claimed to be an aid in the characterisation of the intermolecular forces that are present in solutions and liquid mixtures. Ultrasonic measurements are competitive with other analytical methods and in many cases a unique analytical tool for the characterisation of the quality of liquids and their components, measurement of concentration of liquids, detecting of chemical reactions, phase transitions and other processes. The propagation of sound through liquids is controlled not only by the nature of the molecular structure of the molecules but also by the effects of the basic shape of the molecules on the intermolecular interactions. The measurement of ultrasonic velocity enables the accurate determination of isentropic compressibility coefficient. This coefficient is adiabatic because the compressions and decompressions in ultrasonic waves in liquids are too fast for heat dissipation. As a second derivative of thermodynamic potentials, compressibility is extremely sensitive to the structure and intermolecular interactions in liquids. From the primary data, various thermodynamic parameters can be calculated which are sensitive to interaction between solute and solvent. Knowledge of these mixing properties has relevance in both theoretical and applied areas of research because such results are useful in the general design and simulation process.

The properties of carboxamides have been the subject of considerable interest because of the versatility of these compounds as solvents and their close relationship to many structural problems in molecular biology. The cyclic amides (lactams) are very interesting compounds as they have carbon and nitrogen of a peptide bond linked by a ring composed of methylene groups. Owing to its donor-acceptor properties, it can interact with other amide molecules via hydrogen bond. In this way, lactam provide small molecular models for the amide group in peptides, polypeptides and proteins. Self-association\textsuperscript{1-6} of (Z) lactams also serves as a bases in nucleic amides. Of particular interest is the compound γ-butyrolactam (n = 5) i.e. pyrrolidin-2-one (PY), which is a highly polar non-aqueous solvent.
Hexamethylphosphortriamide (HMPA) is a dipolar, aprotic, nonhydroxylic solvent with excellent solvent properties having high dielectric permittivity ($\varepsilon = 30.54$) and high dipole moment ($\mu = 5.39$ D). It has some interesting biological properties: it is a model compound for the study of certain anti-cancer (cytostatic) drugs and the general mechanism of chemosterilation. The oxygen atom of $P=O$ group in HMPA is a very efficient proton acceptor, e.g., toward OH protons such as in alkanols. The polar or double bond character of the $P=O$ bond varies according to other substituents; 50% ionic character must be assumed in HMPA. It is an excellent solvent for performing SnAr reactions quickly.

A search of the literature reveals that thermodynamic studies on the binary mixtures involving PY or HMPA are rather scarce. Keeping in view of their importance, it was desired to study and analyze the mixtures of interesting compounds with PY or HMPA. The investigation is expected to throw light into the various types of interactions operating in mixtures. The other components chosen on the basis of their academic and technical importance are:

**Halogenated alkanol:** Alkanols are relatively poor proton-donors, but highly electronegative substitutes increase their proton-donating ability. Replacement of H by halo atom in the alkyl group of an alkanol has shown a significant effect on the dispersion interactions in mixtures. The halogenated alkanol are also associated but to a lesser degree in comparison to normal alkanol. These are interesting solvents of industrial importance but there are only few reports which concern the study of excess thermodynamic functions of mixtures involving halogenated alkanol.

**Aromatic hydrocarbons:** Isomeric xylenes (o-, m-, p-) and ethylbenzene form an interesting group of compounds in which the shapes of the molecules can be changed without any appreciable change in size. These aromatic hydrocarbons are inert nonpolar solvents and are of immense industrial importance.

**Cyano compounds:** Nitriles are important industrial solvents and have a wide range of technological applications. Acetonitrile, propionitrile, butyronitrile, valeronitrile and benzonitrile are self-associated liquids and have high dipole moments. They are not good proton acceptors and as the heteroassociation weakens, the self-association becomes stronger. Our choice of nitrile series has been guided by a regular varying molecular size of...
selected nitriles without inordinate alteration in molecular structure and the effective polarity of nitriles.

Glycols: Ethylene glycol and three oligomers\textsuperscript{32} of ethylene glycol, di-, tri- and tetraethylene glycol are used as polar heads on a variety of non-ionic surfactants and their physicochemical characterisation is important in understanding the interactions leading to the micellization processes.

Tritons: The non-ionic surfactants, Tritons are widely used in biological work such as separation of proteins from cell membranes\textsuperscript{33} and also in drug formulation\textsuperscript{34} because of little or no physiological side effects by the surfactant. Information about physicochemical properties of Tritons in solvents is therefore necessary for understanding of the system itself.

As a contribution towards a more comprehensive thermodynamic description, and to illustrate how mixing of solvent/surfactant affects the behaviour of thermodynamic properties of liquid mixtures containing PY or HMPA as one of the component, excess volume and ultrasonic velocity of mixtures of PY with halogenated alkanol or aromatic hydrocarbons or cyano compounds or glycols or Tritons and HMPA with halogenated alkanol have been measured and analyzed. The aim of the study is two fold: first is to enlarge the thermodynamic data base for mixtures needed by the industry for design purpose. Secondly, the estimation of several related parameters in order to attain a deeper insight into various interactions operating in the mixtures. The ultrasonic velocity data has been used to estimate the isentropic compressibility and its excess value $K_f^E$. Since the compressibility coefficient is a measure of the relative change in volume with pressure it seems appropriate to examine the variation of $K_f^E$ as a function of mole fraction of PY or HMPA in the binary mixtures. The magnitude and sign of excess quantities are a reflection of the type of interactions taking place in the mixture. A number of factors may contribute to the values of the excess functions of mixtures. Some of these factors are self-association of the component molecules and the change in the extent and strength of the hydrogen bonding when the mixture is formed, orientational order, interstitial accommodation of the component within the other component structure, disruption of associated structure on mixing components and the relative sizes of the component molecules. The values of the excess properties result from balance between these contributions and the relative
importance of the various contributions depends on the property under consideration. In
general thermodynamic properties of liquid mixtures containing associated species are
affected by diverse intermolecular effects such as changes in molecular association
equilibria and structural effects arising from differences in size and shape of the
component molecules. The analysis of the data obtained has been carried out by estimating
apparent and partial quantities. The apparent and partial quantities are two important
thermodynamic properties which may be helpful in the identification of interaction in
solutions. These quantities are sensitive to interactions between solute and solvent and to
changes induced in the solvent by the solute as the concentration of the latter tends to zero.
Trends in these properties with changes in temperature and composition offer some
qualitative assessment of solution behaviour in the intermediate composition range.

The version of the Flory model developed by Patterson and coworkers,35-38 the so
called Prigogine-Flory-Patterson (PFP) model has been often used to correlate and to
predict the excess thermodynamic properties i.e. \( V_m^E \), \( H_m^E \) and \( C_{p,m}^E \) etc. for different kind
of mixtures. The PFP model is very useful to analyze the influence of the size, the shape
and the momentum of the molecules on the behaviour of binary mixtures. The analysis of
the prediction have shown the occurrence of "structure creation or destruction". The PFP
theory is applied to predict the sign and magnitude of \( V_m^E \) by taking into account the
different contributions viz. interactional, free volume and P' effect considered in the
theory.

In an attempt to explore the nature of the interactions, various thermo-acoustical
parameters39-48 viz. free volume \( V_f \), specific acoustic impedance \( Z \), solvation number \( S_n \),
relative association \( R_A \), molecular association \( M_A \), Rao's constant \( R \), Wada's constant \( W \),
intermolecular free length \( L_r \), van der Waals constant \( b \), molecular radius \( r \), geometrical
volume \( B \), molar surface area \( Y \) and available volume \( V_a \) have been calculated by
combining ultrasonic velocity and density data (calculated from excess molar volume \( V_m^E \)
data). A number of empirical and theoretical equations47-52 has also been used for the
theoretical prediction of ultrasonic velocity.