Summary

Estimation of Ultrasonic & Thermodynamic Properties of Liquid mixtures

The present thesis represents an overview of the systematic experimental and theoretical research work on the physicochemical properties of associated liquid mixtures. The main objective of the work is to study the associational behavior of liquid mixtures of varied nature, and to extract new information of the interactions between the species existing in these systems on molecular level.

There has been an increasing interest in the study of molecular interactions and a number of experimental techniques have been used to investigate the interactions between the components of binary liquid mixtures. Traditional theories of solutions dwell exclusively on two aspects of liquid mixtures. One of these is the entropy associated with dispersion of the two molecular species or of their constituent elements in case of complex molecules, among one another. A lattice model often serves as the device for estimating this “combinatorial entropy”. The other aspect relates to the interactions between unlike and like neighbors. Treatment of the properties of liquid mixtures has progressed little beyond the level of interpretation possible within the framework supported by these two considerations alone $^{1,2}$. 
More sophisticated treatments\textsuperscript{1-7} of liquid mixtures derived their conceptual basis from (a) the cell model for liquids and (b) the postulations of a universal form for the intermolecular potential.

In the recent years much importance has been given to the behaviour of mixed solvents rather than a single solvent because of their wide range of applications in many chemical industrial and biological processes. The physico-chemical data are often required in many industrial processes (flow, mass transfer or heat transfer calculations, polymerization, solvolysis etc.) and also leads to the formulation of a large no. of methods for correlating or predicting the physical property, composition data. Therefore in view of practical importance of mixed solvents, a deeper knowledge of their solution structure and intermolecular interactions between component molecules at molecular level thus becomes essential. Recently researcher in this field has been focussing their interest more sharply on the molecular structure along with some representative macroscopic property that serves to characterize it.

The composition and temperature dependence of volumetric, acoustic transport and surface properties of associated liquid system provides substantial information of the molecular influence on the intensity of the intermolecular interactions among component molecules and can be used as a powerful tool for studying intermolecular interactions in these systems.
In the present work involves systematic experimental measurement of density, ultrasonic velocity, viscosity, surface tension, and refractive index of benzene, benzonitrile, chlorobenzene, benzyl chloride and benzyl alcohol at 298.15, 303.15, 308.15 and 313.15 K over the entire composition. Number of physico chemical parameters viz. excess functions, thermodynamic properties, acoustical properties and some other properties are derived from these experimental data. These parameters have been used for the qualitative analysis of physicochemical behaviour, nature and number of interactions in the liquid mixtures.

Various workers\textsuperscript{8-22} have proposed several empirical, semi empirical and statistical models for theoretical estimation of the physical properties and their excess functions. Numerous theories have been developed in past for the elucidation of molecular structure and estimation of thermodynamic properties of liquid mixtures. The association phenomenon has been related usually to the deviation of different quantities from additivity and the model in simple averaged geometrical derivations in terms of equilibrium. The associational behaviour of liquids and their correlation with molecular interactions has also been made using three liquid models. This is our first attempt to correlate these models (associated and non-associated in predicting the associational behavior of binary liquid mixtures).
Ramaswami and Anbananthan\textsuperscript{38} proposed the model base on the assumption of linearity of acoustic impedance with the mole fraction of components. Further, Glinski assumed that when solute is added to solvent, the molecules interact according to the equilibrium. By applying the condition of linearity with composition, the observed property can be obtained on comparing the property with the experimental value by changing both the adjustable parameters $K_{as}$ and $\gamma_{ab}$, one can obtain the different values of the sum of squares of deviations. The minimum value of deviation can be obtained theoretically by a pair of the fitted parameter.

Glinski\textsuperscript{39} also predicted the properties by another approach he calculated the observed property by the assumption of linearity of the property with the volume fraction of the component and obtained the deviations. The results obtained by this approach are much better than calculate from Rama Swamy model.

Flory and Coworkers\textsuperscript{11-14} have developed a theory which relates thermodynamic excess properties of liquid mixtures to measurable macroscopic properties of the pure components. In their approach they have included the concepts of degrees of freedom of the component molecules and the ‘$\gamma$’meric structural representation of linear molecules proposed by Prigogine and coworkers\textsuperscript{27-9}. Initially the theory was derived to explain the thermodynamic properties of normal alkane mixtures, and was subsequently extended to encompass systems of
non-polar molecules differing in size and shape. The theory has been applied with varying degrees of success to systems of simple and complex liquid mixtures. An improvement to this theory, the Prigogine-Flory theory, considers excess thermodynamic properties of binary mixtures to be the sum of three contributions, a combinatorial term, an interactional term arising from the difference in chemical nature of the two components and a free volume contribution. More insight into the nature of these contributions has been given by Patterson and his coworkers.

Their approximate equations lead to the separation of these contributions. The excess molar volume can be expressed as: an interactional term which is proportional to the Flory $X_{ij}$ parameter, a free volume contribution which originate from a difference in the degrees of thermal expansion between the two components, and a $P^*$ contribution which arises from the difference in the internal pressures and reduced volumes of components. The approximate form of their excess molar enthalpy equation is divided into a free volume and an interaction contribution.

Prigogine-Flory-Patterson (PFP) theory has been applied to n-alkanes and other mixtures and for calculating various thermodynamic properties of binary mixtures of ionic liquids. Excellent results are also obtained for surface tension, ultrasonic velocity and excess
volumes in case of multicomponent liquid systems. All these examples show the validity of Flory-Patterson theory.

Special interest is given to this statistical theory because of its simplicity and precision in the prediction of various thermodynamic properties. It needs only coefficient of thermal expansion and isothermal compressibility of pure components for computation of many thermodynamic properties. While computing viscosity and excess enthalpy, this theory has an additional advantage over its own procedure of computing sound velocity and surface tension, as no adjustable parameter is required in calculating the former properties.

Theoretical treatment of viscous flow properties of the multicomponent liquid systems on the basis of statistical thermodynamics is a direct consequence of molecular structure of the liquids with special reference to molecular size and shape in terms of different parameters eg. lattice distortion and disorder parameter, condensation effect, steric hindrance contribution, coupling of torsional oscillations and extent of non-ideality arising from shape factor and molecular interaction of the liquid system. There has been a considerable effort at developing interaction information. Heric\textsuperscript{105} and Heric & Brewer\textsuperscript{106} accounted for molecular interactions by dividing the free energy of activation into two parts. One part accounts for the excess free energy of activation, while the other accounts for the ideal free energy of activation. Their discussion of the effect of molecular
size on excess functions gives insight into solution non-ideality and molecular interaction.

Present thesis entitled “Estimation of Ultrasonic & Thermodynamic Properties of Liquid mixture” is divided into six chapters.

First chapter deals with the scope and incentive of the proposed work. Along with the explicit presentation of various approaches employed, a complete literature survey and background of the work is detailed out.

In the Second chapter, experimental techniques, which are being used in the present investigation, have been presented. Respective properties i.e., ultrasonic velocity, viscosity, refractive index are measured at various temperatures with the use of ultrasonic interferometer, Ubleohode viscometer and Abbs refractometer respectively liquid mixtures.

The binary systems under investigation are

i. Benzene+ Benzonitrile

ii. Benzene + Chlorobenzene

iii. Benzene + Benzyl Chloride

iv. Benzene + Benzyl Alcohol

At atmospheric pressure and at 298.15, 303.15, 308.15 and 313.15 K over the entire composition range.
In chapter third, Lorentz-Lorentz relation, Rama Swami & Anbananthan and Gilinski approaches have been used for the temperature dependent study of refractive index of liquid mixtures. In the light of experimental findings, comparative study of three approaches is made. All the models are quite satisfactory with the experimental findings.

In fourth chapter Prigogine-Flory-Patterson theory are employed for the evaluation of theoretical excess volume of liquid binary mixtures at 298.15, 303.15, 308.15 and 313.15 K. Fairly good arrangement have been achieved between theory and experiment.

Chapter fifth deals with prediction of sound velocity of binary liquid mixture. Prigogine-Flory-Patterson, Rama Swami & Anbananthan and Gilinski approach have been employed and comparision has been made. Gelenski model provides good result as compared to other. The average percentage deviation for Gilinski model for for benzene+benzonitrile, benzene+ chlorobenzene, benzene+ benzyl chloride and benzene+ benzyl alcohol at 298.15, 303.15, 308.15 and 313.15 K are found to be $([-3.41, 1.66, 1.77), (-4.62, 1.90, 1.02), (-2.67, 1.52, 1.53)$ and $(-3.33, 1.69, 1.04)]$, $([-1.59, 2.91, 1.49), (-1.39, 1.28, 0.84), (-2.80, 1.52, 2.52)$ and $(-3.43, 2.48, 1.34)]$, $([-3.89, 2.24, 1.29), (-3.62, 2.41, 1.45), (-3.64, 2.17, 1.28)$ and $(-4.38, 2.50, 1.30]$ and $([-5.27, 2.06, 1.24), (-4.18, 1.42, 1.27), (-5.36, 1.94, 1.50)$ and $(-4.99, 2.19, 1.43)]$ respectively.
Six chapter deals with the prediction of associational behavior of binary liquid mixture from viscosity data. Prigogine-Flory-Patterson (PFP) model and Rama Swami and Anbananthan (RS) model have been used for the prediction of viscosity in binary liquid mixture at various temperatures. In this chapter, Redlish-Kister polynomials and standard deviations have been evaluated in order to verify our experimental data. McAlister three body and four body interaction models have also been utilized. The average percentage deviation (APD) for benzene+benzonitrile, benzene+ chlorobenzene, benzene+ benzyl chloride and benzene+ benzyl alcohol at 298.15, 303.15, 308.15 and 313.15 K are [0.04 & 0.4, 0.04 & 0.38, 0.03 & 0.4] and [0.4 & 1.82, 0.37 & 1.74, 0.33 & 1.61] respectively.
References


