Physico-Chemical and Thermodynamic Properties of Binary Liquid Systems

INTRODUCTION (Purpose of the Research)

In chemical industry, the knowledge of thermodynamic and physical properties of liquid mixtures is essential for design calculations involving separations, heat transfer, mass transfer and fluid flow. The exhaustive consultation of the literature reveals that substantial amount of work has been done on ultrasonic velocity, surface tension, refractive index, excess volume and compressibility of binary liquid mixture and is still in progress\textsuperscript{1-17} over a wide range of temperature and pressure. In the proposed work, experimental measurements of ultrasonic velocity, density, surface tension, refractive index and excess volume of binary liquid mixtures would be carried out at various temperature.

The other aim of the present work is to study the excess thermodynamic properties which are the measure of extent of interactions involved in the liquid mixtures. It has been pointed out by several workers that excess thermodynamic functions are sensitively dependent not only on the difference in intermolecular forces but also on the difference in size of the molecule\textsuperscript{18-19}. The study of excess volume and excess compressibility gives important information on intermolecular forces determining the properties of mixture. The interaction between unlike molecules seems to be ascribed to dispersion forces and dipole induced dipole interactions, considering the chemical nature of the species of the system. Excess volume ($V^E$) is expressed as sum of two terms, the one ($V^E_{SIZE}$) is expressed as sum of two terms, the one ($V^E_{SIZE}$) associated with size difference and the other $V^E_{int}$ associated with the interaction forces between molecules. Thus, for a mixture composed of species A,B,C and D we have

$$V^E = V^E_{SIZE} + V^E_{int} \quad (1)$$

$$V^E_{SIZE} = [(V^*_A - V^*_{AA})X_A + (V^*_B - V^*_{BB})X_B + (V^*_C - V^*_{CC})X_C +\ldots$$
\[(V^*_D-V^*_D)X_D \left[1-(9RT/\pi)(V^0/W_M)^{-1}\right]\]  \hspace{1cm} (2)

In the above equation, all the symbols have their usual significance as described in the paper\textsuperscript{20}, Ahluwalia et al.\textsuperscript{21} have given a complete picture of interactions in solutions through partial molar volume.

A very interesting and important aspect of the proposed work is to test the validity and compare the merits of various empirical, semi-empirical and statistical theories of liquid state. The most fascinating statistical mechanical theory of Flory and Ramaswami & Abanantham\textsuperscript{22} would be employed as a tool in the present context. The particular properties which are to be studied are viscosity, refractive index, excess volume density, isotropic and isentropic compressibility, ultrasonic velocity and surface tension. The agreement between theory and experiment would be used as criteria for the success of particular model of a multicomponent system. A unique feature of the proposed work which differs altogether from the normal proposal is the evaluation and prediction of some thermodynamic properties of liquid mixtures over a wide range of temperature and composition from the recent experimental measurements of ultrasonic propagation parameters. The entire work has not so far been done by earlier workers.

Sound velocity in connection with density data have been used to deduce a number of useful thermodynamic properties of pure liquids and their mixtures. Some of the properties of liquid state e.g. isentropic compressibility, isothermal compressibility etc. can not be determined by any other technique. In such cases sound velocity measurements are employed. In addition, ultrasonic velocity and density measurements are convenient and very economical. It is the purpose of the present work to deduce some very useful and interesting thermodynamic properties of liquids and liquid mixtures using the experimental data of sound velocity, density, viscosity, refractive index and surface tension available in literature. The present work involves theoretical deductions based on mathematical formalism. The entire work involves the computation of various thermodynamic properties.
**BRIEF REVIEW OF THE WORK**

Density and viscosity of saturated liquid dimethoxymethane were measured at various temperatures by J.Wu et al\textsuperscript{23}. P.Jain and M.Singh\textsuperscript{24} measured density, viscosity and excess properties of binary liquid mixtures of propylene with polar and non-polar solvents. G.Cruz-Reyes et al\textsuperscript{25} established a correlation of viscosities of pure gases and liquids with the use of significant structure theory. R.J.Martins\textsuperscript{26} interpreted the viscosity of pure liquids at elevated pressures. L.T.Novok\textsuperscript{27} proposed modeling of viscosity of liquid mixtures of polymer solvent systems. Calculations of viscosity of ternary and quaternary liquid mixtures were carried out by several workers\textsuperscript{28}. Excess Gibbs free energy model for calculating the viscosity of binary liquid mixtures is given by R.J.Martins et.al\textsuperscript{29}. Generic van der Waals equation of state, modified free volume theory of diffused viscosity of simple liquids were determined by, Laghaei et. al.\textsuperscript{30}, J.Wu\textsuperscript{31} experimentally determined the viscosity of saturated liquid dimethylether at elevated temperatures. Viscosity of the homologous series of n-(trans-4-n-alkyl cyclohexyl) isothioganate was studied by J.Jadzyn\textsuperscript{32}. Excess molar enthalpies of dimethylcarbonate and (methanol, ethanol, 1-propanol) at various temperatures and pressures were studied by S.Li and H.Dong\textsuperscript{33}. G.C.Shekar and M.V.P.Rao\textsuperscript{34} studied excess molar volumes and speeds of sound of N,N-dimethylacetamide with chloroethane at 303.15 K. C.Valles\textsuperscript{35} measured the excess enthalpy, density, speed of sound and viscosity of 2-methyl tetrahydrobutanol at different temperatures. Generalized correlation for the viscosity of hydrocarbons based on corresponding principles and molar refraction was studied by M.Riazi et al\textsuperscript{36}. Y.-Y.Duan et al\textsuperscript{37} measured the saturated liquid viscosity of cyclopentane and isopentane. A.E. Nasrabad\textsuperscript{38} modified the free volume theory of self-diffusion and molecular theory of shear viscosity of liquid CO\textsubscript{2}. Determination of viscosity and density of di-(2-ethylhexyl) phosphoric acid + kerosene were carried out by L.R.Koekemoer et al\textsuperscript{39}. I. Johnson\textsuperscript{40} experimentally determined density, viscosity and speed of sound in the ternary mixture of 2-ethoxyethane + dimethylformamide + N,N-dimethylacetamide and 2-ethoxyethanol + dimethylformamide + N,N-dimethylacetamide at 308.15 K.
X.-H. et al\textsuperscript{41} measured the density, viscosity and surface tension at 298.15 K and studied the liquid-liquid equilibria at various temperatures under atmospheric pressure for the binary mixture of diethyl ether + water. Densities and viscosities of regular quinary system toluene(1)+ octane(2)+ ethylbenzene (3) + tetradecane(4)+ hexadecane(5) and its quaternary systems were studied by A.-F.A. Asfour and A.H.Nhaesi\textsuperscript{42}. D. Agrawal and M.Singh\textsuperscript{43} measured the densities and viscosities of binary liquid mixtures of trichloroethylene and tetrachloro ethylene with some polar and non-polar solvents. S.Singh et al\textsuperscript{44} measured viscosities, densities and speeds of sound of o-xylene, m-xylene and isopropylbenzene with 4-methylpentan –2- one at 298.15 K. T.Sun and A.S.Teja\textsuperscript{45} determined density, viscosity and thermal conductivity of aqueous benzoic acid mixtures at various temperatures. V.K.Rattan, S.Kapoor and K.Tochigi\textsuperscript{46} measured viscosities and densities of binary mixtures of toluene with acetic acid at various temperatures. Segment based Eyring-NRTL viscosity model for mixtures containing polymers was studied by L.T.Novak et al\textsuperscript{47}. Viscosities, densities and refractive indices of 2,2,4-trimethylbenzene + cyclohexane + decane ternary liquid system were measured by D.Gomez-Diaz et al\textsuperscript{48}. A.S.Pensado et al\textsuperscript{49} used rolling ball viscometer in the determination of dynamic viscosities of 2,3-Dimethyl- pentane at 60 M Pa at different temperatures. Correlations for the density and viscosity of aqueous formaldehyde solutions were studied by J.G.M.Winkelman et al\textsuperscript{50}.

**DETAIL OF HYPOTHESIS/ MODEL/ THEORY/ EXPERIMENT**

Experimental

The proposed work deals with the experimental technique and procedure for the measurement of ultrasonic velocity, viscosity, density, refractive index and excess volume with the help ultrasonic interferometer, common ubbelohde type viscometer, bicapillary pyknomwter, Abbs refractometer and dialtometer respectively over a wide range of composition which are available in our laboratory. Each and every substance are purified before use in accordance with the literature\textsuperscript{51}. All the experiments will be
carried out on a water bath thermostatically controlled for about half an hour before any measurements.

Theoretical

Flory$^{52-54}$ explored a statistical theory of liquids and liquid mixtures, keeping in view the deficiencies and their removal. Starting from a reduced equation of state using simple partition function suitable for liquids e.g.

$$\phi = \phi_{\text{comb}}[\chi(V^{1/3} - V^{*1/3})^3]^{mc} \exp^{-E_0/RT} \quad (1)$$

The reduced equation of state obtained from the resulting partition function is given by

$$\frac{P V}{T} = \frac{V}{(V - 1)} - \frac{1}{V T} \quad (2)$$

Reduced and characteristic parameters have been derived from the above equation.

Ultrasonic velocity has been evaluated with the help of well known Auerbach relation.

$$C = \left(\frac{\sigma}{6.3 \times 10^{-1}}\right)^{2/3} \quad (3)$$

where

$$\sigma = \sigma^* \sigma(V) \quad (4)$$

and

$$\sigma^* = K^{1/3} P^{*2/3} T^{*1/3} \quad (5)$$

and

$$\sigma V = [M V - \frac{(V - 1)y}{2} \ln \left(\frac{V - 0.5}{y - 1/3}\right)] \quad (6)$$

Excess volume is given by the expression

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Excess isothermal compressibility is defined as

$$\beta_T^E = -V^{-1} \left( \frac{\partial V^E}{\partial P} \right)_T = -V^{-1} \left( \frac{\partial V^E}{\partial T} \right)_P$$

or

$$\beta_T^E = \frac{3V^2}{p^*[(V^{-1})^3 - 3 - (\psi_1 V_1 T_1 + \psi_2 V_2 T_2)]}$$

Viscosity of the liquid mixture is given by

$$\ln \eta = -\Delta G_M^R RT + \frac{1}{V^{-1}} - \frac{X_1}{V_1^{-1}} - \frac{X_2}{V_2^{-1}}$$

$$+ X_1 \ln \eta_1 + X_2 \ln \eta_2$$

Theoretical evaluation of refractive index has been carried out with the help of various mixing rules.

Prigogine and Co-workers adhered to the cell model as a guide to formulation of the mean intermolecular energy $E_0$. Quite apart from its intrinsic physical inconsistencies, the cell model is known empirically to lead to an energy which depends much too steeply on the volume. We therefore reject this approach in favour of one suggested by considerations of the radial distribution function. The arguments for this preference have been presented by Hilderbrand and Scott. They have shown that the energy is usually well represented by an expression of the form suggested by Frank

$$E_0 = \text{constant} / V_m$$

Where $m$ may be treated as a constant, usually in the range of 1.0 to 1.5 for non-polar liquids. In interests of restricting the number of parameters permitted, we taken $m=1$, and write

$$E_0 = -Nrs\gamma / 2\eta$$

(11)
Where \( s \) is the number of intermolecular contact sites per segment, \( \eta \) is a constant characterizing the energy of interaction for a pair of neighboring sites, and \( \nu \) finds further justification in the fact that the treatment will generally be applied over only a limited range of volume. Application over wider ranges has been forfeited implicitly in the designation of \( c \) as a constant parameter. At the larger volumes characterizing the liquid near its critical point, for example the number \( e \) of intermolecular degrees of freedom must necessarily decrease.

Also to be noted in the implication of eq.(11) that the intermolecular energy can be reckoned according to the number of contact sites of the area of contact. Short of an inordinately detailed accounting of correlation interactions (London forces) between all intermolecular pairs of atoms in the interacting molecules. This should afford a good approximation for molecules of a complexity not less than that of methane, as was pointed out in the introduction.

The partition function expressed by eq.(1) resembles with that proposed a number of years ago by Hirschfelder and Eyring. It differs from their partition function through introduction of the parameter \( c \), whereby application to liquids comprising non-spherical molecules is made possible. The reduced partition function which follows from eq.(1) and (11) are:

\[
Z = Z_{comb} \left( \gamma \nu^* \right)^{rNc} \left( \nu - 1 \right)^{3rNc} \exp \left( rNc / \nu^* \right)
\]

(12)

and the reduced equation of state

\[
\tilde{\rho} \tilde{\nu} / \tilde{T} = \tilde{\nu}^{-1/3} \left( \tilde{\nu}^{-1/3} - 1 \right) - 1 / \tilde{\nu} \tilde{T}
\]

(13)

Obtained from it are identical with those of the Hirschfelder and Eyring theory. Departures occur however in the definitions of the various reduced quantities changing from molecular to molar units per segment for \( \nu \), \( \nu^* \) and \( \eta \), we have

\[
\tilde{\nu} = \nu / \nu^*
\]

(14)
Thus

\[ p^* = cRT^* / \nu^* \]  \hspace{1cm} (17)

Where 3c is the number of external degrees of freedom per element or segment. The compressibility \( K \) or the thermal pressure coefficient \( \gamma = (\partial p / \partial T)_V \), serve to define \( p^* \) from \( \nu^* \), \( T^* \) and \( p^* \) the set of primary parameters \( \nu^* \) (or \( \nu^* = r \nu^* \)), \( s_n \) and \( c^* \) (or \( C^* \)) can be determined. The fact that the theory presented is approximate cannot be denied. Its purpose namely the treatment of liquid mixtures, precludes an elaborate scheme and it is doubtful that a better representation of liquid state properties can be achieved without disproportionate sacrifice of facility of application. The formulation given should, at the very least, afford a substantial improvement in treating liquid mixtures over ignoring altogether the characteristics of the pure components denoted by their equation of state parameters.

The following analysis is confined to binary mixtures, the components being indexed by subscripts 1 and 2. The molecular element or segment is to be defined in correspondence for the two species such that \( r_1 \) and \( r_2 \) shall be in the ratio of the

\[ \widetilde{T} = T / T^* = 2\nu^* cRT / s \eta \]  \hspace{1cm} (15)

\[ \widetilde{p} = p / p^* = 2p\nu^* \nu^* / s \eta \]  \hspace{1cm} (16)
respective molar core volumes \( v^*_1 \) and \( v^*_2 \). Similarly, \( s_1 \) and \( s_2 \) shall be in the ratio of the molecular surface areas of contact per segment.

Let \( A_{11}, A_{12}, A_{22} \) represent the number of contact pairs between the respective species and let \( \eta_{11}/v \) etc., be the energies associated with each. Then

\[
- E_0 (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})/v
\]

Since

\[
2A_{11} + A_{12} = s_1 r_1 N_1
\]

\[
2A_{22} + A_{12} = s_2 r_2 N_2
\]

It follows that

\[
- E_0 = (s_1 r_1 N_1\eta_{11} + s_2 r_2 N_2\eta_{22} - A_{12}\Delta \eta)/2/v \quad (20)
\]

Where

\[
\Delta \eta = \eta_{11} + \eta_{22} - 2\eta_{12}
\]

Random mixing of the two species will be assumed. As a further approximation, we take the expectation that a species of kind I neighbors any given site to be equal to its site fraction \( \theta \), defined for a binary mixture by

\[
\theta_2 = 1 - \theta_2 s_2 r_2 N_2/srN \quad (21)
\]

The characteristic pressures for the pure components (see eq. 18) are

\[
p^*_1 = s_1 \eta_{11}/2v^*_1; \quad p^*_2 = s_2 \eta_{22}/2v^*_2
\]

The characteristic temperature \( T^* \) for the mixture is given by

\[
1/T^* = \left( \phi_1 P^*_1/T^*_1 + \phi_2 P^*_2/T^*_2 \right) - \left( \phi_1 P^*_1 + \phi_2 P^*_2 \right) - \left( \phi_1 \theta_1 X_{12} \right)^{-1} \quad (23)
\]

Where the characteristic temperature \( T^*_1 \& T^*_2 \) are defined in accordance with eq.(15)

Ignoring the difference between the energy and enthalpy of a condensed system at low pressure, we have for the enthalpy of mixing (i.e. “excess” enthalpy)

\[
\Delta H_M = E_0 \text{ (mixture)} - (E_0 (1) - E_0 (2))
\]

\[
= r N v^* \left[ \phi_1 P^*_1/v_1 + \phi_2 P^*_2/v_2 - p^*/v \right] \quad (24)
\]
This is equivalent in form to the corresponding expression derived for mixtures of n-alkanes. Equations given above allow this result to be expressed in the alternative forms.

\[
\Delta H_M = fN^* \left[ \varphi_1 p_1^* (1/\tilde{\nu}_1 - 1/\tilde{\nu}) + \varphi_2 p_2^* (1/\tilde{\nu}_2 - 1/\tilde{\nu}) + (\varphi_1 \theta_2 / \tilde{\nu}) X_{12} \right] = N_1 p_1^* \nu_1 (1/\tilde{\nu}_1 - 1/\tilde{\nu}) + N_2 p_2^* \nu_2 (1/\tilde{\nu}_2 - 1/\tilde{\nu}) + (N_1 \nu_1 \theta_2 / \tilde{\nu}) X_{12} \quad (25)
\]

the latter equation is preferred for mixtures of molecules of comparable size.

The last term in each of these equations for the mixing enthalpy represents the contributions from contact interactions attributable to a difference between 1,2 pairs and the mean of 1,1 and 2,2 contact pairs. It is the only term normally considered. We designated this term the contact interaction term. The terms preceding it in the mixing enthalpy expressions will be referred to as the equation of state terms. Their contribution depends on the reduced volume of the solution compared to those of the pure components.

**PROPOSED METHODOLOGY OF THE PRESENT RESEARCH WORK**

The entire proposed work would be carried out in different phases in the first phase, complete literature survey will be done. Recent publications on the proposed topic will be collected from different sources. In second phase each and every substance taken for the present investigation will be purified and then tested. Measurements would be carried out for the desired properties after calibration of the instruments.

In the third and final phase of the proposed work is the theoretical evaluation of aforesaid properties with the help of various empirical, semi-empirical and statistical theories and their validity. Theoretical prediction and its comparison with experimental values would be helpful in understanding the interactions involves in the liquid mixtures.

Substantial amount of the work have been done on the measurements of ultrasonic velocity, surface tension, viscosity, refractive index etc. of binary liquid mixtures for
non-polar components over a wide range of composition. But temperature dependent study of these properties for binary systems of associated and polar molecules has become prevalent for the modern chemist and is still in progress. In these molecules, interactions are so violent and strong that it would be a real study of molecular interactions. Density, ultrasonic velocity, viscosity, surface tension and refractive index for different liquid mixtures would be measured at various temperatures and different liquid models would be applied in order to study the interactions involved in these liquid mixtures.

**EXPECTED OUT COME OF THE PROPOSED WORK**

Substantial amount of work have been carried out by several workers on sound velocity, surface tension, viscosity, refractive index and compressibility for binary and multi phase liquid mixtures particularly for non-polar systems. But theoretical prediction of these properties and their applicability could not be made successfully due to scarcity of experimental data. In the proposed work measurements for these properties would be carried out at various temperatures for different polar binary liquid mixtures and different liquid models particularly Prigogine- Flory- Patterson model, would be applied in order to study the interactions in the liquid mixture and also to test the validity of a particular model for such polar binary liquid mixtures comparision between theory and experiment would be treated as the success of a particular model. As far as my knowledge is concerned, no body has applied the particular model for such polar binary liquid mixtures. It is very much expected that the proposed work will prove the theoretical significance and resolve so many questions arising in the mind of physical chemist.
REFERENCES

52. A.Abe and P.J.Flory, J.Am. Chem. Soc., 87, 1838(1965)

Signature of Candidate

Signature of Supervisor
SUMMARY

Liquid state has become a subject of intense study in recent years because of the characteristics of liquids, i.e. the strong interactions of the component molecules and their state of disorder. The knowledge of various thermodynamic and physical properties of multicomponent liquid mixtures is essential for design calculations involving heat transfer, mass transfer and fluid flow. There are two principal reasons for the great amount of experimental and theoretical work on the properties of liquid mixtures [1]. The first is that they provide a way of studying the physical forces acting between the two molecules of different species, and second for the study of mixtures, is the appearance of new phenomenon (interactions) which are not present in pure liquids. The most interesting of these are new types of phase equilibrium [2] which arises from extra degree of freedom introduced by possibility of varying the properties of components. Traditional theories of solutions dwell exclusively on two aspects of liquid mixtures. One of these is the entropy associated with dispersion of the low 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 neighboring molecules and in particular, to the difference in interactions between unlike and like neighbor pairs. 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 [3, 4]. The equilibrium properties of a liquid has strongly dependent on what may be loosely called its local structure, often expressed in terms such as packing
density, free volume or more exactly in terms of the radial distribution function in as such as, this local structure depends on the force between molecules and volume of the molecules, in general, it is well change with composition, this change in turn will be reflected in the thermodynamic properties of the mixture. Contribution of this nature has either been ignored altogether or correction to a state of null volume change on mixing has been adopted as a means of compensating for the effect referred [5]. It wills apparent, however, that adjustment of one thermodynamic quantity (eg. volume in this manner) will not in general, affect a simultaneous correction of others (eg the free energy of that part of it relating to the local structure) to their linearly interpolated values. The choice of volume as the property to be conserved is arbitrary and there is assurance that nullity of volume change obviates consideration of other characteristic properties of the liquid.

Substantial amount of work on thermodynamic and physico-chemical properties of liquid mixtures have been done by many workers assuming two body interactions with the aid of Lennard-Jones Devonshire interacting potential which ascribed to each pair elements called contact pair, the intermolecular energy is usually discussed in terms of the familiar Lennard-Jones potential operating between the molecular centres. Even in comparatively simple polyatomic molecules, the acentric distribution of polarizable electrons necessitates fairly drastic modification of this potential. Kihara [6], Hamann and Lambert [7] and Pitzer [8, 9] have offered modified intermolecular potentials for polyatomic molecules, especially those approximating spherical symmetry in form. An extension [10] of these considerations which suggests itself, as a basis for treating the intermolecular energy in liquid
consists in integrating the interactions of elements of the core of one molecule with the elements of all surrounding molecules, these latter being treated as occupying the space outside the cavity reserved for the molecule in question. The result obtained departs markedly from the form of the intermolecular energy according to the theory of Lennard-Jones and Devonshire. Numerous theories have been developed in past [11-16] to study the properties of and interactions in liquid solutions. Flory and coworkers [17-20] 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 ‘γ’meric structural representation of linear molecules proposed by Prigogine and coworkers [21-23]. The theory was initially 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 [24-28]. 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 [29-32]. 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. The theory of Prigogine-Flory-Patterson (PFP) has been applied to n-alkanes and other mixtures [11, 12, 30-33]. The success of Flory-Patterson theory has also been achieved for calculating various thermodynamic properties of binary mixtures of ionic liquids [34-36] and liquid metals [37]. Surprisingly, this theory has been found to give excellent results for surface tension [38-41], ultrasonic velocity [14-16, 37-45] and excess volumes in case of multicomponent liquid mixture. This statistical theory is of special interest on account of its simplicity and precision in the prediction of various thermodynamic properties. Coefficient of thermal expansion and the isothermal compressibility are the only parameters of pure components which are needed 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. However, PFP model does not give good result when strong interactions are involved in liquid mixtures. There have been used a number of experimental techniques to study the molecular interactions taking place in the liquid mixture and the ultrasonic speed and thermodynamic data derived from it have been widely used for this purpose, measurement of sound velocity offers a convenient method for determining certain thermodynamic properties of liquid not easily obtained by other means.
Ultrasonic investigations of liquid mixture are of considerable importance in understanding intermolecular interactions between the component molecules. It is clear that the concentration independence of sound velocity should reflect the structural arrangements occurring in the liquid mixture. Relations between association phenomena in liquids and sound velocity in them were analyzed a long time ago by Schaafs [46,47] and Jacobson [48,49]. Ramaswamy and Anbanthan [50] proposed a model based on the assumption of linearity of acoustical impedance with mole fractions of components, the acoustical impedance, according to Kinsler et al [51], has greater significance as a parameter describing a medium and intermolecular interaction than does ultrasonic velocity and density individually. The model of Ramaswamy and Anbanthan can be further simplified by equation assuming additivity of the time of transmission of acoustic signal with the volume fractions of the components derived by Natta and Baccaredda [52] and the theory was finally proposed by Glinski [53]. The model gave much more reliable results for interacting liquids.

Viscosity of multicomponent liquid mixtures is of considerable physico-chemical interest and is essential in designing calculation involving heat transfer, mass transfer and fluid flow. The knowledge of viscosity is widely used in processing and product formulation in many industrial applications. An exhaustive literature survey reveals that recently, it has been applied in the study of mass transfer in a rotating packed bed with viscous Newtonian and non-Newtonian fluid [54], in the use of nanoliter viscometer for analyzing blood plasma and other liquid samples [55]. A large amount of work has been done on the experimental measurements of viscosity of single component [56-57] and binary liquid mixture [58-
In addition to experimental findings, a number of models have also been reported which include the models for calculating viscosity of pure liquids at high pressure [60], calculation of ternary liquid mixture [61], modified free volume theory [62] etc.

The prediction of surface tension is of outstanding importance in many scientific and technological areas such as; liquid-liquid extraction, distillation, environmental sciences, material sciences and plays a significant role in many industries such as paint, detergents, agrochemicals and petroleum.

An exhaustive literature survey reveals that surface tension is helpful in the study of foaming [63], interfacial energy [64], adsorption [65], surfactant [66] etc. Substantial amount of work has been reported on experimental measurement of surface tension of binary [67-68] and ternary [69-70] liquid mixture. due to wide applicability of the surface tension of liquid mixtures in various areas, it is worth while to predict theoretically the surface tension of binary liquid mixtures from the values of pure components. Substantial amount of work has been done and still in progress on the application of various models. Average potential theory of Prigogine [71], Prigogine [72], Parallel layer theory, Flory [73], Sanchez [74] and others for the calculation of surface tension of binary liquid mixtures.

Refractive index is a fundamental physical property of a substance, which is often used to identify a particular substance, confirm its purity, or measurement its concentration. It is commonly used to measure the concentration of solute in an aqueous solution. The predictions of refractive index of multicomponent liquid mixtures are essential for many physico-chemical calculations. Various theoretical mixing rules for
refractive index of binary liquid mixtures have been examined and tested in detail by Heller[75], while scrutinizing the relative merits and interrelation of Lorentz-Lorentz (L-L), Glad Stone- Dole (GD), Wiener (W), Arago-biot (AB) relation, he proposed a mixing rules for determining the refractive index of binary liquid mixtures have been tested by Aminabhavi [76] and it was found that the Lorentz-Lorentz (L-L), Gladstone-Dole (GD), Wiener (W) and Arago-Biot (AB) relations, performed considerably well, with the experimental precision.

Present thesis entitled “Physico-Chemical and Thermodynamic Properties of Binary Liquid Systems” is divided in 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. Experimental techniques, which are being used in our research, have been presented in the second chapter. Density, ultrasonic velocity of two binary liquid mixture viz 1-Butanol+Dodecane and 2-Butanol+Dodecane at four different temperatures, 288.15, 298.15, 308.15 and 318.15 K were determined. Where as density, viscosity, surface tension and refractive index of three binary liquid mixtures, viz 2-Propanol + Benzyl alcohol, 2-Propanol + 2-Phenyl ethanol and Benzyl alcohol + 2-Phenyl ethanol at three different temperatures 298.15, 308.15 and 318.15 K were determined. Chapter third deals with the application of Prigogine-Flory-Patterson (PFP) theory and Ramaswamy, Glinski, McAllister three body and McAllister four body interaction models for the evaluation of absolute ultrasonic velocity and acoustic impedance for two binary liquid mixtures at four different temperatures. The validity of experimental data was
tested by Redlish-Kister approach [77] and McAllister multibody interaction models [78]. The agreement between experimental and Ramaswamy was found satisfactory. The standard deviation ($\sigma$) from Redlich Kister equation was found to lie between 0.23 ms$^{-1}$ and 0.53 ms$^{-1}$. It was observed that the four body model of McAllister correlated to ultrasonic velocity and acoustic impedance for binary liquid mixtures corresponds to significantly higher degree of accuracy than the three body model the average percentage deviation (APD) for ultrasonic velocities in PFP, Ramaswamy, Glinski, McAllister three body and McAllister 4 body models are found to be (1.07,0.04,0.22,0.05,0.02 at 288.15 K), (2.07, 0.14, 0.36, 0.04, 0.02 at 298.15 K), (0.29,0.23,0.52,0.04,0.02 at 308.15 K) and (1.85,0.15,1.15,0.04,0.01 at 318.15 K) for 1-Butanol+Dodecane and (1.30,0.20,0.37,0.07,0.03 at 288.15K), (1.83,0.24,0.63,0.06,0.03 at 298.15K), (0.40,0.26,0.90,0.05,0.03 at 308.15K) and (2.13, 0.10, 0.82, 0.03,0.12 at 318.15 K) for 2-Butanol+Dodecane respectively. Considerable good results in Ramaswamy, Glinski, and McAllister three body and McAllister 4 body models are obtained as compared to PFP model indicate good fitting. Higher values of percentage deviation for PFP model were explained as model was developed for non-electrolyte γ-meric spherical chain molecules and the systems under investigation have interacting and associating properties. The average percentage deviation (APD) for acoustic impedance in PFP, Ramaswamy, Glinski, McAllister three body and McAllister 4 body models were found to be (1.07,1.36,1.53,0.02,0.02 at 288.15 K), (2.07,1.49,1.69,0.02,0.02 at 298.15 K), (0.29,1.62,1.88,0.02,0.02 at 308.15 K) and (1.85,1.28,2.55,0.02,0.02 at 318.15 K) for 1-Butanol+Dodecane and (1.30,1.00,1.61,0.04,0.02 at 288.15K), (1.80,1.00,1.92,0.03,0.03 at
In fourth chapter Prigogine-Flory-Patterson (PFP) model along with Ramaswamy, Glinski and McAllister three bodies and McAllister four body models are applied for the evaluation of viscosity of three binary liquid mixtures at three different temperatures. The Redlich Kister approach and McAllister multibody interaction models are used to test the validity of experimental data. The $\sigma$ values of Redlick Kister equation were found to lie between 0.005 mPa.s and 0.021 mPa.s and the largest value corresponds to Benzyl alcohol+2-Phenyl ethanol at 308.15 K for all other systems, the $\sigma$ values lies under precision requirements. A higher degree of correlation was achieved by four body model of McAllister equation for all the system than three body model. The maximum value of standard deviation ($\sigma$) occurred as 0.084 mPa.s for McAllister three body and 0.040 mPa.s for McAllister four body. The average percentage deviation (APD) for viscosity in PFP, Ramaswamy, Glinski, McAllister 3 body and McAllister 4 body models were found to be (1.80, 0.58, 3.92, 0.60, 0.25 at 298.15 K), (2.44, 0.85, 2.70, 0.62, 1.08 at 308.15 K), (4.13, 0.65, 0.28, 0.78, 0.92 at 318.15 K) for 2-Propenol + Benzyl alcohol, (9.53, 1.23, 23.84, 1.23, 0.51 at 298.15 K), (7.75, 0.47, 19.17, 0.59, 0.56 at 308.15 K), (8.93, 2.06, 12.96, 0.39, 1.08 at 318.15 K) for 2-Propenol +2-Phenyl ethanol and (2.18, 0.23, 2.54, 0.16, 0.25 at 298.15 K), (5.25, 0.87, 9.35, 0.19, 0.14 at 308.15 K) and (5.25, 0.87, 9.35, 0.16, 0.09 at 318.15 K) for Benzyl alcohol+ 2-Phenyl ethanol. A very less percentage deviation in Ramaswamy model indicate good fitting. It was also observed that all other models i.e. Glinski, McAllister three body and McAllister four body interaction models also produced
good results, which again signify the utility and applicability of these models. Higher values of percentage deviation for PFP model in comparison to Ramaswamy model can be explained as the model was developed for non-electrolyte γ-meric spherical chain molecule and the system under investigation have an interacting and associating property. First time PFP model is applied to associated binary liquid mixtures; good results are obtained up to some extent. However, there is every possibility to improve the result. In general, still modifications are needed in order to interpret the associational behaviour and interactions in liquid mixtures.

Fifth chapter deals with the application of Prigogine-Flory-Patterson (PFP), Ramaswamy, Glinski, McAllister three bodies and McAllister four body models for the evaluation of surface tension of three binary liquid mixtures at three different temperatures. Redlich Kister approach along with McAllister multibody interaction models are used to test the validity of experimental data. The standard deviation $\sigma$ from Redlich Kister equation was found to lie between 0.016 dyne/cm$^2$ and 0.323 dyne/cm$^2$. The largest value of standard deviation ($\sigma$) corresponds to 2-Propenol+Benzyl alcohol at 318.15 K. Benzyl alcohol+2-Phenyl ethanol consist of very small standard deviation in comparison to other two binary liquid mixtures. McAllister four body interaction models corresponds to the highest value of standard deviation for 2-Propenol+ 2-Phenyl ethanol is 0.52 dyne/cm$^2$ at 308.15 K and the lowest value for Benzyl alcohol+2-Phenyl ethanol is 0.05 dyne/cm$^2$ at 298.15 K. The average percentage deviation (APD) for surface tension in PFP, Ramaswamy, Glinski, McAllister three body and McAllister four body interaction models were found to be (5.60,4.61,6.92,0.51,0.14 at 298.15
where as for Benzyl alcohol+ 2-Phenyl ethanol the average percentage deviation (APD) was found to be (9.90,2.38,3.92,0.09,0.20 at 298.15 K), (7.84,1.03,2.35,0.15,0.19 at 308.15 K) and (5.75,0.49,1.58,0.18,0.14 at 318.15 K). The overall percentage deviations are less in Ramaswamy, Glinski, McAllister three body and McAllister four body interaction model than PFP model for Benzyl alcohol+2-Phenyl ethanol in comparison to 2-Propenol+Benzyl alcohol and 2-Propenol+2-Phenyl ethanol. Considerable good results in Ramaswamy, Glinski, McAllister three bodies (Mc3) and McAllister four bodies (Mc4) interaction model as compared to PFP model indicate good fitting. Considerable good result in Ramaswamy model indicate the formation of associates, it was also observed that all other models i.e. Glinski, McAllister three body and McAllister four body models also produced good results, which again signify the utility and the applicability of these models. Higher values of percentage deviations for PFP model can be explained as the model was developed for non-electrolyte γ-meric spherical chain molecules and the system under investigation have interacting and associating property.

The last sixth chapter deals with the application of Lorentz-Lorentz (L-L) relation, Ramaswamy, Glinski, McAllister three body and four body models for the evaluation of refractive index for three binary liquid mixtures at three different temperatures. The standard deviation (\(\sigma\)) values from Redlich Kister polynomial were found to lie between 0.000001 and 0.25970. The largest value of standard deviation (\(\sigma\))
corresponds to Benzyl alcohol+2-Phenyl ethanol at 318.15 K. The maximum standard deviation ($\sigma$) value occurred as 0.00279 for McAllister three body and 0.09056 for McAllister four body interaction model. It can be also observed that McAllister four body interaction models correlated to the refractive index of binary liquid mixtures to significantly higher degree of accuracy for all the system. The average percentage deviation (APD) for refractive indices in L-L, Ramaswamy, Glinski, McAllister three body and McAllister four body interaction model were found be (0.0484, 8.2583, 8.5597, 0.0786, 0.0029 at 298.15 K), (0.0587, 7.6849, 7.6928, 0.0857, 0.0057 at 308.15 K), (0.0692, 7.0561, 6.7571, 0.0935, 5.5078 at 318.15 K) for 2-Propenol + Benzyl alcohol, (0.0905, 9.1089, 8.9736, 0.1557, 0.0077 at 298.15 K), (0.0989, 8.5022, 8.282, 0.1680, 0.0068 at 308.15 K), (0.1092, 7.9748, 7.3628, 0.1776, 0.0125 at 318.15 K) for 2-Propenol +2-Phenyl ethanol and (0.1266, 2.9771, 2.9880, 0.0008, 0.0038 at 298.15 K), (0.1407, 1.6484, 1.5661, 0.0032, 0.0081 at 308.15 K) and (0.1530, 1.0499, 0.9423, 0.4238, 0.0063 at 318.15 K) for Benzyl alcohol+ 2-Phenyl ethanol. A very less percentage deviation in Ramaswamy, Glinski, McAllister three body and McAllister four body interaction model along with Lorentz-Lorentz relation for Benzyl alcohol +2-Phenyl ethanol indicate good fitting. However it was observed that the overall percentage deviation were less in Lorentz- Lorentz (L-L) than Ramaswamy and Glinski model for almost all binary system. Good results of Ramaswamy and Glinski models clearly indicated the success of theory and formation of associate in the liquid mixture.
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