

## **CHAPTER I**

### **Introduction**

Industrial revolution both energized and freshly unleashed an increased use of scientifically produced knowledge in industrial productions. Like for any other branch of scientific knowledge, increased knowledge of chemistry as a science and technology appear to be increasingly used by chemical industry for the production of consumables and allied products. Ever-growing demand of newer chemicals, their synthesis and their hitherto unknown effects came to be emphatically observed in biophysical processes both in the natural world and in the human body. Until quite recently the adverse effects of such newer chemicals and their concentrations remained unnoticed and the chemical industries in this regard remained in a state of inertia. However, with the emergent public criticisms through media and political debates on such impacts of newly discovered or synthesized chemicals and their concentrates and more particularly the solvents with multiple uses and high volume productions, the chemical industry began to respond to such impacts in line with the standards set for environmental protection and public health and safety by regimes at multiple levels both locally and globally. The utilities of such solvents and chemicals and their syntheses in the broader human welfare require differentiation of such solvents, identification of their fundamental properties and the prior understanding of their risks and utilities. Therefore, the proper selection of suitable solvents becomes necessary and for this the knowledge of solution properties is very essential. Especially the thermodynamic and transport properties are required to make proper selection of these solvents. Naturally it is seen that matter exists in a state of mixtures in an overwhelming manner and hence the possibility of existence of pure substances is a rarity. Liquid-liquid mixtures uniquely exhibit such unusual behavior bereft of pure substances, thereby attracting the attention of scientists and scholars to undertake studies on liquid and liquid mixtures. Thus the physico-chemical behavior and the nature of the molecular interactions in the multi-component liquid mixtures has been a major subject of interest from the point of view of their applications in many branches of science such as pharmaceutical industries, polymer industries, cosmetic industries, molecular biology, *etc.* The non-aqueous systems have been of immense importance

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to the technologist and theoretician as many chemical processes occur in these systems.<sup>1,2</sup>

The classification of different organic solvents are based on the types of organic groups, donor-acceptor properties,<sup>3,4</sup> hydrogen bonding,<sup>5</sup> hard and soft acid base properties,<sup>6</sup> and dielectric constants, *etc.* As a result the different solvent shows a wide divergence in properties that ultimately influence their thermodynamic, transport, acoustic and optical properties, especially when they are mixed to give a homogeneous mixture. The study of such properties in solvent mixtures (binary/ternary/quaternary) would thus provide important information for understanding solvent-solvent interactions. Knowledge of the nature of intermolecular interactions amongst the mixed components can be had from rheological<sup>7</sup> and thermodynamic study of physico-chemical properties of solvent-solvent systems.<sup>8,9</sup> That's why various experimental data on thermodynamic, acoustic, transport and optical properties of pure liquid and liquid mixtures are of significant importance to understand the intermolecular forces and in testing the theories which attempt to estimate the mixture properties. The prediction of the properties of a multi-component (binary/ternary/quaternary) liquid mixtures can be made either from pure component properties as developed by Eyring,<sup>10</sup> Flory *et al.*,<sup>11-17</sup> or from the properties of their contributing binary systems as advanced by Bertrand *et al.*,<sup>18,19</sup> The theoretical as well as experimental estimation of the different parameters such as density, viscosity, ultrasonic speed and refractive indices of the pure components and their mixtures have been extensively used both as qualitatively and quantitatively to predict the changes in the volume, viscosity, speed of sound, *etc.*, and the extent of complex formation when different organic solvents are mixed. Such changes in the properties of the mixed solvents arise as a result of several contributions like combinational, energetic, molecular orientation, free volume, steric hindrance, *etc.* If the polar components are involved the additional contribution like hydrogen bonding, dipole-induced dipole, disruption of molecular order due to dipole-dipole interactions come into play. The interstitial accommodation due to different size and large difference in molar volume also leads to such changes. The interpretation of such properties has been made with the introduction of several solution theories of liquid and liquid mixtures of non-electrolytic components. Prigogine and co-workers<sup>20-23</sup> employed the cell model of liquid state put forward by Eyring *et al.*<sup>10,24,25</sup> in correlating the

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thermodynamic properties of liquid mixtures with intermolecular energy parameters. They assumed random mixing of the components and showed that the thermodynamic excess functions are affected only to a small extent when the molecules are of same size. Prigogine and Bellemans<sup>26</sup> extended this theory to liquid mixtures assuming the cells of two sizes exist in liquid mixtures. This model failed to predict the correct values of the thermodynamic functions for any liquid. As a result of this, a number of theories have been developed based on the theorem of corresponding states.<sup>27</sup> Like the cell model theory, Flory and co-workers<sup>14-17,28,29</sup> developed a theory that relates the thermodynamic excess properties of liquid mixtures to measurable macroscopic properties of the pure components. Patterson and Delmas<sup>30,31</sup> analysed the theory proposed by Prigogine and Flory and found that Flory theory was superior to those originally proposed by Prigogine and collaborator<sup>20-23</sup> using their average potential cell model. In more general form, the Prigogine-Flory-Patterson (PFP) theory has been successfully employed to binary liquid mixtures to estimate the combinational contribution, free volume contribution, interaction contribution and the various thermodynamic properties of the binary mixtures. This theory has also been applied to calculate surface tension,<sup>32-35</sup> ultrasonic speeds of sound<sup>32-39</sup> and viscosities<sup>40-43</sup> of the liquid mixtures satisfactorily.

### 1.1. Solvent Effects

Most of the chemical and biological processes occur in solution phase. The role of solvation in chemistry and biology is obvious. The influence of the solvent on chemical phenomena has received the attention of researchers from both experimental and theoretical fields related to chemistry. A solvent can influence the interaction of the local environment with the individual species undergoing the reactions and thus also influences the outcome of a chemical reaction. The solvent, on one level, provides an energy path for the stabilization of energetic products formed during reactions and also provides physical barriers to the motion of the reactive species. On a more subtle level, the solvent perturbs the potential energy curves that govern these reactions.<sup>44</sup> Since the solvent species around a solute form a structure that determines the outcome of chemical and/or biological events, the solvent species are not just “spectator” species rather they are part of the chemical or biochemical process. Solvation has been proved to be of fundamental importance in diverse areas like biological activities and atmospheric processes.<sup>45</sup> Solvated ions appear in high

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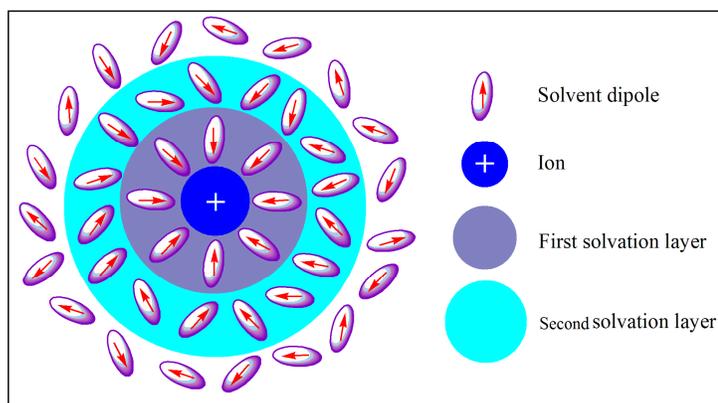
concentrations in living organisms where their presence or absence can fundamentally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common<sup>46</sup> and the exchange of solvent molecules around ions in solutions is fundamental in understanding the reactivity of ions in solution.<sup>47</sup> Solvated ions also play a key role in electrochemical applications simply because the conductivity of electrolytes depend on the ion-solvent interactions.<sup>48</sup> Majority of the chemical reactions are usually performed in solutions and solvents can influence reactions in a number of ways. Solvents may be used as a reaction medium to bring reactants together, as a reactant to react with a solute to make it soluble and as a carrier to deliver chemical compounds in solutions to their point of use in the required amounts.

Solvents also control the temperature in exothermic and endothermic reactions. In endothermic reactions, heat could be supplied through a heated inert solvent having a high heat capacity while in exothermic reactions, the surplus heat can be removed by allowing the solvent to boil or absorb heat. If reactions involve solid reactants, solvents could be used to create a homogenous reaction phase (*i.e.*, solution) through which the solid reactants can be brought into contact. It is important to select the most appropriate solvent so as to get most effective results or optimum yield of the products. A good solvent should be able to meet all the necessary standards such as it should be an inert to all the reaction conditions, the boiling point of the solvent should be appropriate, at the end of the reaction there should not be any difficulty in its removal and it should dissolve the reagents and reactants. In essence, the reaction rates are influenced by differential solvation of the starting material and the transition state by the solvent. When the molecules of the reactant start moving towards the transition state, the molecules of the solvent orient themselves and render the transition state stable. Greater the extent of stability of the transition state compared to the starting material, faster the reaction proceeds and vice-versa. However, in practice a differential solvation is realized if the solvent undergoes rapid relaxation or re-orientation to the ground state orientation from the transition state orientation. So reactions involving weakly dipolar solvents that are rapidly relaxing with a tendency for having sharp barriers exhibit equilibrium solvent effects.

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### 1.1.1. Solvation

Solvation is basically the process of association through interactions of the solvent molecules with the solute molecules or ions. A solvated complex is formed when the solute molecules or ions dissolve in a solvent, spread out and become surrounded by the molecules of the solvent. Alternatively solvation refers to surrounding of the solute molecules or ions by solvent molecules. The region around a solute, up to which the solvent molecules are reoriented due to the force created by the solute, is known as solvation shell or cybotactic region. Figure 1.1 shows a typical solvation shell and how the solvent molecules orient themselves to form the solvation shell. Three types of intermolecular attractive forces are relevant to the solvation process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure 1.2, the process of solvation may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as solvation). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the overall dissolution process will release or absorb energy.

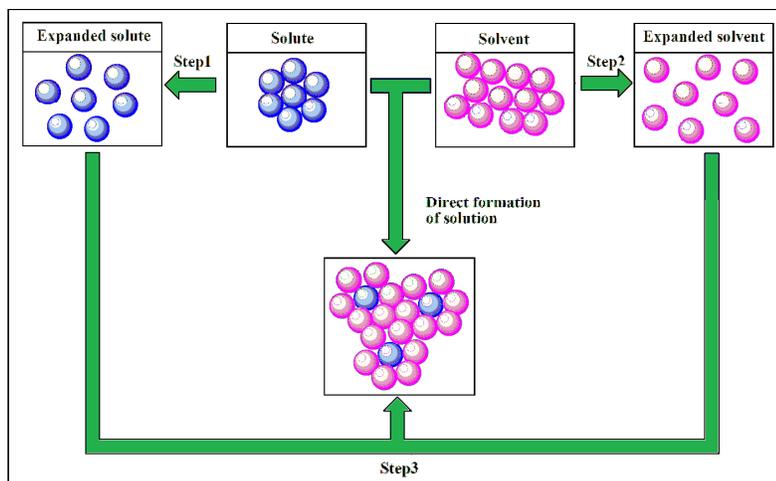


**Fig 1.1.** A schematic representation of solvation shell

For solvation to occur, energy is required to release individual ions or molecules from the lattice in which they are present. This is necessary to break the attractions that the ions have with each other and is equal to the lattice free energy. The energy released in the process of solvation is called the free energy of solvation. If the liberated solvation energy is lower than the lattice energy, the overall dissolution process is endothermic and if the solvation energy is higher than the lattice energy, the overall

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process is exothermic. For the spontaneity of the dissolving process the dissolution process should be endothermic.

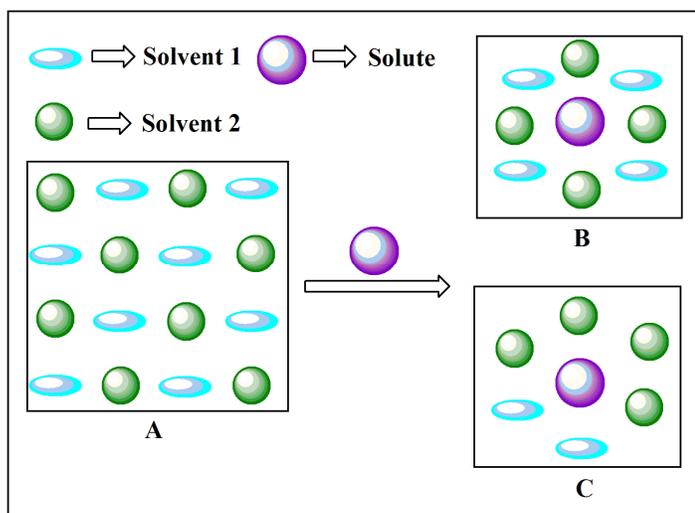


**Fig. 1.2.** Stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation of a solute in a solvent (Step 3).

### 1.1.2. Preferential Solvation

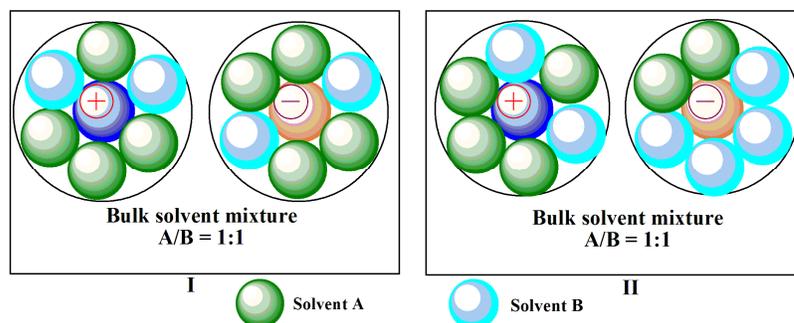
In the mixtures containing two or more solvents the solvation process is more complicated as compared to pure solvent. It is observed that an increase in the number of component molecules in the mixture increases the number of the solute-solvent interactions. Besides the intermolecular interactions between the solute-solvent molecules in the mixtures, the interactions amongst the unlike solvent molecules play a vital role leading to a large departure from ideal behaviour as expected from the Raoult's law of depression of vapour pressure. In order to understand how the solvent composition affects the solute behavior, we need to know the composition that the solute has in its immediate vicinity different from the bulk composition of the mixed solvent. The solute is surrounded preferably by the component of the mixture, which leads to more negative Gibb's free energy of solvation. The observation that the solvent shell has a composition other than the macroscopic ratio is termed as selective solvation or preferential solvation.<sup>49</sup> If one of the solvent of the mixture is practically excluded from the solvation shell of the solute then it is regarded as selective solvation. This phenomenon is represented in Figure 1.3.

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**Fig. 1.3.** Schematic representation of preferential solvation, A: mixture of solvent 1 and solvent 2 in 1:1 composition; B: ideal solvation of the solute; C: preferential solvation of the solute by solvent 1.

These terms are generally used to describe the molecular microscopic local solute-induced inhomogeneity in a multi-component solvent mixture. They include both (i) non-specific solute/solvent association caused by dielectric enrichment in the solvent shell of solute, ions or dipolar solute molecules and (ii) specific solute/solvent association such as hydrogen-bonding or electron pair donor/electron pair acceptor interactions.



**Fig. 1.4.** Schematic model for the selective solvation of ions by one component of a binary 1:1 mixture of the solvents A and B: (I), Homoselective solvation; (II), heteroselective solvation.

Homoselective solvation occurs when both the ions of a dissolved molecule or salt are solvated preferentially by the same solvent in a mixture of two solvents and heteroselective solvation occurs when the preferential solvation of the cation by one, and the anion by the other solvent (Figure 1.4).

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### 1.2. Importance and Scope of the Physico-Chemical Parameters

Density and viscosity of liquid mixtures are indispensable physical parameters, required in most engineering calculations where fluid flow of mixture is an important factor and are essential in the design processes involving chemical separations, equipment design, heat transfer, fluid flow and molecular dynamics, *etc.* The knowledge of the dependence of these parameters on composition is of great interest from a theoretical stand point, since it may lead to better understanding of the fundamental behavior; for instance the molecular interactions among the components of the liquid mixture. Such behavior and their change with composition and temperature are generally studied by estimating the different physico-chemical and thermodynamic properties. Among the different thermodynamic parameters the excess or deviation parameters gives better understanding of the molecular interactions. The density and the related volumetric properties such as excess molar volume and apparent molar volume are of great importance in characterizing such behavior and structural aspects of solutions. Though viscosity is not a thermodynamic parameter but still is of great importance in many chemical disciplines and commercial applications. The deviation in viscosity provides a proper understanding of molecular motions and interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents.<sup>50,51</sup> The other thermodynamic parameters such as excess free energy of activation of viscous flow, excess enthalpy and excess entropy can also be evaluated using experimental density and viscosity. These excess parameters are also important in estimating the molecular interactions in the liquid mixtures of variable compositions and temperature. The sign and magnitude of these excess parameters imparts estimate of strength of unlike interactions in the binary, ternary, *etc.*, solvent systems.

The experimental viscosity data are valuable for testing the different theories and empirical relations such as Grunberg and Nissan,<sup>52</sup> Hind *et al.*,<sup>53</sup> Heric-Brewer,<sup>54</sup> Katti and Chaudhri<sup>55</sup> and McAllister,<sup>56</sup> *etc.*, for liquid mixtures. Apart from these, viscosity models based on Eyring theory coupled with Peng-Robinson cubic equation of state for non-ideal liquid mixtures<sup>57</sup> and Bloomfield-Dewan model,<sup>58</sup> a relation between viscosity and thermodynamic properties of mixing on the basis of absolute reaction rate are used to correlate and estimate the viscosities of non-ideal liquid mixtures under experimental temperature with different compositions.

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Amongst the different methods used, ultrasonic method is found to be sensitive and reliable; thus this method has been used by many researchers to explain the molecular interactions in pure liquids as well as in liquid mixtures. Prior to the application of ultrasonic methods to mixtures/solutions, the spectroscopic, dielectric techniques, excess molar volume and viscosity deviations, *etc.*, were only the tool to study the nature and strength of molecular interactions. However, the application of ultrasonic methods has made possible not only the evaluation of physico-chemical properties of the mixtures/solutions but also more reliability on the interpretation of molecular interactions. Therefore, in the present study the experimental speed of sound and density data are used to evaluate acoustic and thermodynamic parameters such as isentropic compressibility, intermolecular free length, specific acoustic impedance, free volume and internal pressure. These parameters are found to be very sensitive to molecular interactions<sup>59-62</sup> but the excess properties of these parameters provide better understanding of the nature and strength of molecular interactions and are sensitive to molecular forces as well as the size of the molecules.<sup>63</sup> Furthermore, the density and ultrasonic sound speed are valuable tools to develop new theoretical models and learn about the liquid state.<sup>64</sup> It is observed that a number of workers have extensively applied various empirical and semi-empirical theories to study the ultrasonic speeds in binary and ternary mixtures. Among them the commonly used theories are Nomoto relation (NOM),<sup>65</sup> Schaaff's collision factor theory (CFT),<sup>66,67</sup> Impedance dependence relation (IDR),<sup>68</sup> Vandael Vangeal Ideal mixture relation (IMR),<sup>69</sup> Jacobson's Free Length Theory (FLT),<sup>70,71</sup> Junjie's equation (JUN)<sup>72</sup> and Flory's theory,<sup>14</sup> *etc.* Theoretical evaluation of ultrasonic speed in binary liquid mixtures and its correlation to study the molecular interaction has been successfully performed in recent years<sup>73-82</sup> using the above theoretical relations. The refractive index is one of the important physical properties of liquid and liquid mixtures and is being increasingly used as a tool<sup>83-87</sup> for the investigation of the nature of intermolecular interaction between the liquid mixture constituents. Knowledge of refractive index of multi-component mixtures provides information regarding the interactions in these mixtures.<sup>88-90</sup> Pandey *et al.*<sup>91</sup> have made refractive index measurements in liquid mixtures and have suggested that such studies are very much helpful for understanding the molecular interactions in the components of the mixture. Refractive indices can also be used to estimate the different elastic properties of the molecule from which the type of

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molecular interactions can be very well understood.<sup>92</sup> In addition to binary liquid mixtures, a few ternary<sup>93,94</sup> and quaternary mixtures<sup>95</sup> have also been studied employing refractive index measurements. Prediction of refractive index of multi-component liquid mixtures theoretically is essential for many physico-chemical calculations that include correlation of refractive index with density.<sup>96-98</sup> A number of empirical/semi-empirical mixing rules and models has been suggested by different researchers to correlate the experimental refractive index of the liquid mixtures. Some of the common mixing rules used are Lorentz-Lorentz relation,<sup>99,100</sup> Gladstone-Dale,<sup>101</sup> Arago-Biot,<sup>102</sup> Weiner model,<sup>103</sup> Eyring-John,<sup>104</sup> Heller,<sup>105</sup> Eykman,<sup>106</sup> and Newton,<sup>107</sup> *etc.*

### 1.3. Objective and Application of the Research work

The study of physico-chemical properties involving excess or deviation properties as well as the other derived thermodynamic parameters play an important role in understanding the structure and many molecular interactions amongst the molecules of the components in liquid mixture. These properties can provide a precise knowledge about the behavior of the molecules on mixing. It is also seen that the results of one experimental technique often contradicts the results obtained from some other technique; therefore attempts has been made using more than one technique to establish the nature and strength of molecular interactions. With this approach the precise correlation between the microscopic structure and macroscopic properties can be establish. In the present thesis, emphasis has been laid mainly on the measurements of four physical properties, *viz.*, density, viscosity, speed of sound and refractive index of the liquid mixtures (binary, ternary and quaternary) containing: (i) cyclohexane and cyclohexanone with some esters like methyl acetate, ethyl acetate and methyl salicylate, (ii) 1,4-dioxane and 2-ethyl-1-hexanol with ethylenediamine, 1,2-dichloroethane and monoethanolamine at varying temperatures covering the entire composition range. These solvents have drawn much attention of the scientists due to their varied industrial applications.<sup>108-118</sup> Therefore the main objectives of the present dissertation are:

- i) to study the molecular interactions through various physico-chemical and derived parameters like excess or deviation properties (such as excess molar volumes and viscosity deviation, *etc.*) in various selected solvent systems.

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- ii) to enrich the physico-chemical database of properties of the components and their mixtures (binary, ternary and quaternary liquid mixtures).
- iii) To employ experimental or derived data to critically test some of the empirical and semi-empirical models (involving volume, viscosity, ultrasonic speed and refractive index) and compare their predictive capabilities.

So, a number of parameters such as excess molar volume, partial molar volume, viscosity deviation, isentropic compressibility, excess isentropic compressibility, intermolecular free length, acoustic impedance, free volume, internal pressure and molar refraction, *etc.*, were derived using measured experimental (density, viscosity, ultrasonic speed and refractive index) data for each set of liquid mixtures. The above mentioned parameters, particularly the excess or deviation functions, were found to be very sensitive to the intermolecular interactions between the unlike components of a mixture. Again the model approach has several immediate advantages. The empirical and semi-empirical models often help in understanding these interactions in terms of individual component properties as well as offer a visual picture and hence provide a physical explanation for a variety of phenomenon operating in liquids and liquid mixtures. In this context Peng-Robinson equation of states, Flory and Proggone-Flory-Patterson theories were applied to analyse the excess molar volumes ( $V_m^E$ ). The viscosity data were correlated with models like Grunberg and Nissan, Hind, Heric-Brewer, Katti and Chaudhri and McAllister, *etc.*, for liquid mixtures. Apart from these, a viscosity model based on Eyring theory coupled with Peng-Robinson cubic equation of state for non-ideal liquid mixtures and Bloomfield-Dewan model were tested. The experimental speeds of sound have been analysed in terms of Nomoto relation, Schaaff's collision factor theory, Impedance dependence relation, Vandael Vangeal Ideal mixture relation, Jacobson's Free Length Theory, Junjie's equation and Flory's theory, *etc.* The experimental refractive indices and molar refractions were correlated in terms of various mixing rules, *viz.*, Lorentz-Lorenz, Gladstone-Dale, Arago-Biot, Eykman, Wiener and Heller relations, *etc.* Relative merits of these mixing rules have been discussed in terms of standard deviation or root mean square percent deviations (RMSD%). The nature of molecular interactions observed in

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different solvent systems also corroborated with structural changes and substantiated by the infrared spectroscopic study<sup>119</sup> of the respective solvent systems.

### 1.4. Importance of Solvents and Solvent Mixtures Studied

1,4-dioxane, 2-ethyl-1-hexanol, 1,2-disubstituted ethanes (*viz.*, ethylenediamine, 1,2-dichloroethane, monoethanolamine), cyclohexane, cyclohexanone and some alkyl acetates (*viz.*, methyl acetate, ethyl acetate and methyl salicylate) were chosen as the subject liquids in the works embodied in this dissertation. The study of these solvents and their mixtures is of immense interest because of their wide application as solvents and solubilizing agents in many industries like pharmaceutical, cosmetics, *etc.* 1,4-dioxane is very hygroscopic and miscible in all proportions with water. It is a non-polar, aprotic, non-hydrogen bonded cyclic diether and finds numerous applications in organic syntheses and industrial processes as a solvent for saturated and unsaturated hydrocarbons<sup>120</sup> as well as in the high-energy battery technology.<sup>121</sup> Ethylenediamine is a strongly basic colorless liquid with ammonia like odour and reacts readily with moisture in humid air to produce a corrosive, toxic and irritating mist. It is an important raw material for the production of polymers, pharmaceuticals, pesticides, herbicides and dye fixing agent. It is widely used as bleach activators, chelating agents, corrosion inhibitors, elastomeric fibers, plastic lubricants, polyamide resins, rubber processing additives, lube oil and fuel additives. 1,2-dichloroethane, commonly known as ethylene dichloride, is a colourless liquid with chloroform like odour. It is a  $\sigma$ -acceptor and is used as a solvent, degreaser, as a precursor for the synthesis of other chemical agents. It is also used in the production of vinyl chloride which is used to make a variety of plastic and vinyl products including polyvinyl chloride (PVC) pipes, furniture and automobile upholstery, wall coverings, house wares, and automobile parts, *etc.*<sup>122</sup> Its other uses include: as a solvent for resins and fats, photography, photocopying, cosmetics, drugs and as a fumigant for grains and orchards. Monoethanolamine is a colourless, viscous liquid with an odour reminiscent to that of ammonia and is a compound containing both primary amine and a primary alcohol. It is used in cement to enhance strength, reduce drying time and protect against the affects of freezing and thawing; metal working fluids to neutralize acid components in lubricants, prevent corrosion, rusting and biocides; in personal care products to make ethanolamine based

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soaps for use in hand lotions, cosmetic creams, cleansing creams, shaving creams, and shampoos; also for dry-cleaning solvents and heavy-duty liquid laundry detergents, in printing inks to control the pH; also used in the purification of petroleum, as a remover of H<sub>2</sub>S and CO<sub>2</sub> from refinery and natural gas streams and as an ingredient in paints and pharmaceuticals.<sup>123</sup> 2-ethyl-1-hexanol is a colourless branched chiral alcohol. It is poorly soluble in water but soluble in most organic solvents. It is produced in bulk for use in multiple applications, say for instance, as solvents, as flavors and fragrances. It is also used as a precursor for the production of other chemicals like the plasticizers and emollients. It is encountered in natural plant fragrances and the odour has been reported as "heavy earthy and slightly floral" for the R-enantiomer and "light sweet floral fragrance" for the S-enantiomer.<sup>124</sup> Its main application is as a feedstock in the manufacture of low-volatility esters, the most important of which is di-(2-ethylhexyl) phthalate, an all purpose plasticizer for PVC and vinyl chloride copolymers. Cyclohexane is a cycloparaffinic non-polar, unassociated, inert hydrocarbon with globular structure<sup>125</sup> with petroleum like odour. It is used in industrial adhesive formulations in particular non-toluene formulation. Nearly all the cyclohexane is consumed in the production of cyclohexanol and cyclohexanone which are then used as a raw material for the industrial production of two important intermediates (*viz.*, adipic acid and caprolactam)<sup>118</sup> used in the production of intermediates for nylon, which has a variety of common applications such as clothing, tents, carpets as well as thermoplastics. Other use of cyclohexane includes various solvent applications and recently has been substituted for benzene in many applications. Cyclohexanone is a colourless oily liquid with acetone like odour and consists of six carbon cyclic structure as well as a ketone functional group. Over time, the liquid may assume yellow colour due to oxidation. It is slightly soluble in water and miscible with common organic solvents. It is used in organic synthesis, particularly in the production of adipic acid and caprolactam, polyvinyl chloride and its copolymers, methacrylate ester polymers, cyclohexanone resins, cyclohexanone oxime, caprolactam and nylon.<sup>118</sup> Additional uses include paint and varnish removers, spot remover, degreasing of metals, polishes, levelling agents, dyeing and delustering silk, lubricating oil additives, solvent for herbicides, natural and synthetic resins, waxes, fats, insecticides, *etc.* Esters exist as a dipolar associates in their pure state.<sup>126</sup> Methyl acetate, also known as methyl ethanoate, is a

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carboxylate ester. It is a flammable liquid with a characteristically pleasant smell reminiscent of some glues and nail polish removers. Ethyl acetate, also known as ethyl ethanoate, is a colorless liquid with a characteristic sweet smell. Both the aliphatic esters methyl acetate and ethyl acetate are commonly used as solvents in glues, nail polish remover, *etc.* Methyl acetate is also used as a solvent for polyurethane coatings and adhesives, blowing agent for polyurethane and other foams intermediates, as paint strippers, fuel system cleaners and additives, battery electrolytes, polymerization solvents, cleaners for electronics and precision parts, *etc.* Ethyl acetate is used to decaffeinate coffee beans and tea leaves also used in paints as an activator or hardener, as a solvent and diluent. Methyl salicylate, also known as oil of wintergreen, is a phenolic ester having strong intramolecular hydrogen bond between its hydroxyl and carbonyl group.<sup>127</sup> It is naturally produced by many species of plants, particularly wintergreens. It is also synthetically produced and used as a fragrance, in foods and beverages and in liniments. This compound is mainly used for relieving muscle aches and pains when applied externally to the affected area. The increasing use of the above mentioned solvents and their mixtures in many industrial processes have greatly stimulated the need for extensive information on their various properties.

### 1.5. Literature Review

Multi-component liquid mixtures were being investigated over the years in terms of various thermodynamics, acoustic, transport and allied properties. So the literature is vast and extensive. Therefore the literature review has been kept confined to some important works that dealt with the liquids and liquid mixtures related to those liquids or liquid mixtures studied in the present dissertation.

Azhagiri *et al.*<sup>128</sup> measured the densities and ultrasonic speeds of the binary mixtures of benzaldehyde with *n*-hexane and cyclohexane over the entire composition range at 30 °C. Various acoustic parameters indicated association amongst the molecules of the mixtures through dipole–dipole interactions. Further, theoretical values of the ultrasonic speeds for binaries were evaluated using several theories and empirical relations. Sinha *et al.*<sup>129</sup> measured the densities, viscosities and ultrasonic speeds for the binary mixtures of some alkoxyethanols and amines in cyclohexanone over the entire range of composition at 298.15 K. The large negative excess molar

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volumes indicated the presence of strong intermolecular hydrogen bond interactions between the amine and the cyclohexanone molecules. But alkoxyethanols systems are characterized by the presence of weak intermolecular interactions probably due to the formation of intramolecular associates *via* the interaction of the etheric oxygen and hydrogen of –OH group in the same alkoxyethanol molecule. Farhan *et al.*<sup>130</sup> reported the densities, viscosities and refractive indices for binary mixtures: (i) cyclohexane + n-decane and (ii) cyclohexane + 1-pentanol over the whole mole fraction range at several temperatures. From these results, excess molar volumes, viscosity deviations and excess refractive indices were calculated. Derived excess or deviation properties suggested that the globular cyclohexane disturbs the orientation order in n-alkanes and hydrogen bond interactions in alkanols and thus resulted into less packed structure. The same group<sup>131</sup> also reported the densities, viscosities and refractive indices for the ternary mixtures: i) cyclohexane + 1-pentanol + n-hexane and ii) cyclohexane + 3-hexanol + n-hexane at  $T = (298.15-328.15)$  K. For the ternary mixture (i), the excess molar volumes were negative at high mole fraction of n-hexane and become positive at low mole fraction of n-hexane but for the ternary mixture (ii), the excess molar volumes were negative over the whole mole fraction range indicating the orientation order and packed structure in these mixtures. Rathnam *et al.*<sup>132</sup> reported the densities, viscosities and refractive indices for the binary mixtures of diethylmalonate with ketones (*viz.*, acetophenone, cyclopentanone, cyclohexanone and 3-pentanone) over the entire composition range at  $T = (303.15-313.15)$  K. Various excess or deviation properties were interpreted in terms of molecular interactions and were also fitted to the Redlich–Kister polynomial equation. Furthermore, different empirical relations were used to correlate the binary mixture viscosities and refractive indices. Malek *et al.*<sup>133</sup> reported the densities, speeds of sound, molar isentropic compressibilities and thermal expansion coefficients for the binary mixtures: (i) cyclohexane + benzene and (ii) cyclohexane + benzaldehyde at  $T = (293.15-323.15)$  K over the entire range of composition at atmospheric pressure. Various results indicated enhancement of molecular order in the (cyclohexane + benzene) mixture through closer molecular packing. But results for the (cyclohexane + benzaldehyde) mixture indicated the breaking of dipole-dipole and  $\pi$ - $\pi$  interactions in benzaldehyde by addition of globular cyclohexane molecules. Gowrisankar *et al.*<sup>134</sup> reported the densities, viscosities and ultrasonic speeds of methyl isobutylketone,

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diethylketone, cyclopentanone, cyclohexanone, 2-methyl cyclohexanone and those of their binary mixtures with N-methyl aniline over the entire composition range at 303.15 K. Various excess or deviation properties like excess molar volumes, excess isentropic compressibility, *etc.*, were discussed in terms of dipole-dipole interactions, interstitial accommodation and hydrogen bond interactions for these binaries. Kannappan *et al.*<sup>135</sup> studied four ternary mixtures of 1-propanol, 1-butanol, 1-pentanol and 1-hexanol with N, N-dimethylformamide and cyclohexanone at several temperatures to characterize the molecular interactions in these systems. Results such as the excess free volume, excess internal pressure and Gibb's free energy, *etc.*, revealed the mixtures to be characterized by dipole-dipole interactions and rupture of hydrogen bond interactions in the pure components. Also excess free volumes of the mixtures suggested that association between 1-alkanols with N, N-dimethylformamide is more than those with cyclohexanone. Roy *et al.*<sup>136</sup> reported densities, viscosities and derived parameters for the ternary mixtures of some alkyl esters with cyclohexane and cyclohexanone and related binary mixtures at 298.15 K under atmospheric pressure. Results such as the excess molar volumes and viscosity deviations suggested that specific interactions for the alkyl acetates with cyclohexane and cyclohexanone increase as the chain length of the acetates increase and non-homogeneity prevails in the ternary mixtures. Venis *et al.*<sup>137</sup> reported the densities, viscosities and ultrasonic speeds for the ternary mixture involving morpholine + cyclohexanone + 1-hexanol at 308.15 K and 318.15 K over the entire range of mole fraction. Parameters like excess molar volume, adiabatic compressibility and free volume, *etc.*, revealed the presence of strong intermolecular interactions between the constituent liquids in the mixtures, chiefly due to strong hydrogen bonding between 1-hexanol and morpholine and electron donor – acceptor complex formation nature of cyclohexanone and geometrical fitting between mixing liquids. The same group<sup>138</sup> has also reported the densities, viscosities and ultrasonic speeds for the ternary mixture involving anisole + cyclohexanone + 1-hexanol over the entire range of mole fraction at 308.15 and 318.15 K. Various derived excess or deviation properties suggested the presence of non-specific physical interactions and unfavorable interactions between the unlike molecules and it was suggested that bond breaking or breaking of liquid order predominates over other type of molecular interactions between the mixing components. Aravinthraj *et al.*<sup>139</sup> reported the densities, viscosities and ultrasonic

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speeds for three ternary liquid mixtures: (i) p-cresol + cyclohexane + formaldehyde, (ii) p-cresol + cyclohexane + acetaldehyde and (iii) p-cresol + cyclohexane + benzaldehyde at  $T = (303-323)$  K. Various derived acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure, *etc.*, revealed the occurrence of dipole-dipole interactions and molecular association through intermolecular hydrogen bonding in these ternary mixtures and significant interactions occur only after introduction of p-cresol in these mixtures. This is due to the intermolecular hydrogen bonding between carbonyl oxygen of aldehydes with hydroxyl hydrogen in p-cresol and dipole-dipole interactions between the same compounds with carbonyl carbon of aldehydes and hydroxyl oxygen. Mistry *et al.*<sup>140</sup> reported the densities, viscosities and ultrasonic speeds for the ternary mixtures of toluene + cyclohexane + nitrobenzene over the entire range of composition at 308 K and calculated various acoustic parameters like adiabatic compressibility, free length and free volume, *etc.* Based on these results it was suggested that there exists dipole-induced dipole interactions between nitrobenzene and cyclohexane and the donor-acceptor complex between toluene and nitrobenzene molecules. Vanathi *et al.*<sup>141</sup> reported densities, viscosities and ultrasonic speeds for the ternary mixture of toluene + chloroform + cyclohexane at  $T = (303.15-313.15)$  K. Various acoustic parameters such as adiabatic compressibility, intermolecular free length, free volume and internal pressure, *etc.*, were derived using the experimental data and it was found that strong intermolecular interactions (association) exist between the components in the mixtures, *i.e.*, greater solute-solvent interactions than solute-solute interactions. Dey *et al.*<sup>113</sup> reported the ultrasonic speeds for four binary, one ternary and one quaternary liquid mixture consisting of cyclohexane, benzene, n-hexane and n-decane at 298.15K. Computation of ultrasonic speeds by various approaches, *i.e.*, van Deal, Nomoto, Junjie and Collision factor theory, *etc.*, were carried out for the six mixtures. A comparative study of the merits of the different approaches has been carried out and all the mixing rules used gave reasonably good results for ultrasonic speeds for the binary as well as the multi-component mixtures. They<sup>142</sup> also reported the viscosities of the above referred mixtures at 298.15 K and estimated viscosities of these solutions by various empirical and semi-empirical models such as McAllister 3 and 4 body, Grunberg-Nissan, Wijk, Hind, Katti-Chaudhri and Tamura-Kurata, *etc.* Sharma *et al.*<sup>143</sup> reported the densities and speeds of sound for ternary mixtures of o-

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chlorotoluene + tetrahydropyran + N-methylformamide or N, N-dimethylformamide or cyclohexane and their sub-binary mixtures at  $T = (298.15-308.15)$  K and  $P = 0.1$  MPa. The excess molar volumes and excess isentropic compressibilities for ternary and binary mixtures were discussed in terms of molecular interactions. The thermodynamic properties were also analyzed in terms of Graph and Prigogine–Flory–Patterson (PFP) theories. S. Kumar *et al.*<sup>144</sup> reported the excess molar volumes for the binary mixtures of 1,4-dioxane with some formamides and anilines over entire composition range at 308.15 K. The excess molar volumes were also rationalized by Graph theoretical arguments, which has further yielded information about the state of association in aniline, formamide and N, N-dimethylformamide. The existence of molecular interactions in these mixtures has also been supported by their infrared spectral studies. The same group<sup>145</sup> has also reported speeds of sound, isentropic and excess isentropic compressibilities of 1,3-dioxolane or 1,4-dioxane + benzene or toluene + formamide or N, N-dimethylformamide ternary and their sub-binary mixtures at 308.15 K and analyzed the excess isentropic compressibilities of the mixtures by Graph and Flory theories. Jangra *et al.*<sup>146</sup> reported the excess molar volumes for the ternary mixtures consisting of 1,4-dioxane + o-toluidine + benzene or toluene or m- or p-xylene as a function of composition at 308.15 K. The resulting excess molar volumes were fitted to Redlich-Kister polynomial to evaluate ternary adjustable parameters and corresponding standard deviations. The observed excess molar volumes were also analyzed in terms of Graph and PFP theories. Bedare *et al.*<sup>147</sup> reported the densities, viscosities and ultrasonic speeds for the binary systems of 1,4-dioxane with ethanol and methanol over the whole range of composition at 308 K. Various acoustic parameters such as adiabatic compressibility, intermolecular free length, free volume and internal pressure were calculated and discussed in terms of molecular interactions between the components of the mixtures. Sinha *et al.*<sup>148</sup> reported the densities and viscosities of binary mixtures consisting of tetrahydrofuran, 1,3-dioxolane and 1,4-dioxane with N, N-dimethylformamide over the entire range of composition at 298.15, 308.15 and 318.15 K. Based on the nature and magnitude of various excess functions and other derived parameters, the molecular interactions in the binary mixtures were primarily attributed to dipole-dipole or dipole-induced dipole interactions. The excess molar volumes as a function of composition at ambient temperature and atmospheric pressure were used to test the applicability of

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PFP theory to the experimental binaries. Bhatia *et al.*<sup>149</sup> reported the densities and ultrasonic speeds of binary mixtures of hexan-1-ol with 1,2-dichloroethane, 1,2-dibromoethane, and 1,1,2,2-tetrachloroethene at several temperatures over the entire range of composition. From these data, the excess molar volumes, deviations of ultrasonic speed, excess molar isentropic compressibility, intermolecular free lengths, mean molecular radii and thermal expansion coefficients were calculated. The positive excess molar volumes at all temperatures for these mixtures over the whole composition range in conjunction with the excess molar isentropic compressibilities and intermolecular free lengths for the studied mixtures confirmed that the hydrogen bond interactions of the type  $\text{Cl}\cdots\text{H}-\text{O}$ ,  $\text{Br}\cdots\text{H}-\text{O}$ ,  $\pi\cdots\text{H}$  and weak physical intermolecular interactions between hexan-1-ol and the halohydrocarbons dominate over the structure-breaking effect of hexan-1-ol on the addition of halohydrocarbons. Kumar *et al.*<sup>150</sup> reported the densities and ultrasonic speeds for the binary mixtures of p-xylene with 1,2-dichloroethane over the different range of composition at 303.15 K. Various excess properties were discussed in terms of the molecular interactions between the components of the mixture and it was suggested that mixing of p-xylene with 1,2-dichloroethane disrupted the dispersive interactions amongst the 1,2-dichloroethane molecules and the mixture is characterized by the presence of specific interactions amongst the dissimilar molecules. They<sup>151</sup> also reported the densities, ultrasonic speeds, excess molar volumes and excess enthalpies for the binary mixture of benzene and 1,2-dichloroethane over the entire composition range at 303.15 K. It is found that intermolecular interactions present in the binary mixtures were stronger than pure solvent-solvent interactions. Observed negative excess molar volumes and positive excess molar enthalpies confirmed the presence of specific chemical attractive forces between the two liquids in the mixture. Kondaiah *et al.*<sup>152</sup> reported the densities, the excess molar volumes and related volumetric properties for the binary mixtures: (i) 1,2-dichloroethane + N, N-dimethylformamide, (ii) 1,2-dichloroethane + dimethylsulphoxide, (iii) dichloromethane + N, N-dimethylformamide and (iv) dichloromethane + dimethylsulphoxide at 308.15 K. The variations of excess properties with composition of the mixtures revealed that hydrogen bond formation between the unlike molecules, dipole-dipole interactions and interstitial accommodation of the unlike molecules were the factors for the

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observed molecular interactions. Ranjbar *et al.*<sup>153</sup> measured the densities and viscosities of binary and ternary liquid mixtures consisting of 1-propanol, benzaldehyde and 1,2-dichloroethane at several temperatures over entire composition range under atmospheric pressure. The interpreted negative viscosity deviations qualitatively by considering the strength of intermolecular hydrogen bonding, molecular size and shapes of the components and suggested that the OH-Cl and OH-O interactions increase the viscosity for the studied mixtures but the effect is not as important as the breaking of associations. Dean *et al.*<sup>154</sup> measured densities and ultrasonic speeds for the binary mixtures of four aliphatic alcohols with monoethanolamine over the entire composition range at several temperatures. Volumetric and acoustic properties of aliphatic alcohols with monoethanolamine were found to depend on the hydrophobicity and hydrogen bonding ability of the alcohols and alcohols with higher hydrophobic character interact more strongly with monoethanolamine. Yasmin *et al.*<sup>111</sup> reported the densities, viscosities, ultrasonic speeds and refractive indices of binary mixtures of poly(ethylene glycol) 200 with ethanolamine, m-cresol and aniline over the entire composition range at 298.15 K under atmospheric pressure. The different excess parameters derived were explained in terms of specific intermolecular and intramolecular interactions present in the mixtures. The stronger interactions in the binary mixture of poly (ethylene glycol) 200 with ethanolamine than with m-cresol and least with aniline were attributed to the hydrogen bond interactions between  $-NH_2$  or  $-OH$  groups in ethanolamine,  $-OH$  group in m-cresol and  $-NH_2$  group in aniline with the hydroxyl groups at the chain terminals of poly (ethylene glycol) 200 molecules. Blanco *et al.*<sup>155</sup> reported the density, viscosity and speed of sound for the ternary mixture consisting of N-methyl-2-pyrrolidone + ethanolamine + water over the entire composition range at several temperatures under a pressure of  $10^5$  Pa. Various excess or deviation properties were then derived and discussed in terms of molecular interactions. The negative excess molar volumes and excess isentropic compressibilities suggested that the present mixture has a more compact structure as compared to the pure component liquids due to the hydrogen bond interactions. Li *et al.*<sup>156</sup> determined the densities and viscosities for the binary mixtures consisting of 1,2-diaminoethane + 1,2-ethanediol over the whole concentration range at (298.15-308.15) K and molecular interactions in the mixtures were interpreted in terms of excess molar volumes. Tumberphale *et al.*<sup>112</sup>

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reported densities, viscosities and ultrasonic speeds for the binary mixtures of n-propyl alcohol with ethylenediamine at 303 K. Different excess properties were discussed in terms of intermolecular interactions between the unlike components in the mixture. Vasudha *et al.*<sup>157</sup> reported the densities and viscosities for the binary mixtures of 2-propanol with methyl acetate, ethyl acetate, butyl acetate and iso-amyl acetate over the entire range of composition at 303.15 K. The derived excess properties revealed that the degree of molecular interactions between dissimilar molecules in the mixtures increase as the chain length of the alkyl acetates increases. S. Sharma *et al.*<sup>158</sup> reported the densities, viscosities and speeds of sound for binary mixtures of oleic acid with methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate over the entire composition range at several temperatures under atmospheric pressure. Various excess properties suggested that the interactions in these mixtures are due to dipole-dipole type forces originating from the polarizability of ester molecules by the dipoles of oleic acid molecules and it was found that as the chain length in esters increases structure-making effect precedes the structure breaking effect for these binary mixtures. Karuna Kumar *et al.*<sup>159</sup> reported the densities, the ultrasonic speeds and excess molar volume and excess isentropic compressibility, *etc.*, the binary mixtures consisting of N-methyl-2-pyrrolidone, methyl acetate, ethyl acetate, butyl acetate over the entire range of composition at  $T = (303.15-318.15)$  K. Various thermo-acoustic results suggested that molecular interactions are due to differences in free volumes between the unlike molecules, dipole-dipole and dipole-induced dipole interactions between unlike molecules. The FTIR spectra of these liquid mixtures also supported the presence of interactions between unlike molecules. The temperature effect on the shapes of the interacting molecules in the binary mixture was also analyzed with the scaled particle theory. Cunha *et al.*<sup>160</sup> reported new experimental data of speeds of sound and densities for seven pure components of pyrolysis bio-oil at atmospheric pressure for several phenols (phenol, o-, m-, and p-cresol), two phenolic ethers (2-methoxyphenol and eugenol) and one phenolic ester (methyl salicylate) at  $T = (288.15-343.15)$  K. They correlated measured densities and sound speeds with PFP theory. Kareem *et al.*<sup>161</sup> reported the densities, refractive indices, viscosities and derived parameters like the excess molar volumes, excess refractive indices and excess viscosities for quaternary mixtures: i) cyclohexane + n-heptane + n-decane + n-hexane and ii) cyclohexane + 1-pentanol + 3-hexanol + n-

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hexane at the temperature range (298.15- 328.15) K. The derived parameters were found to be fluctuating between positive and negative values from ideal ones depending on the nature of molecular interactions in these mixtures. Such behavior was attributed to the interstitial accommodation of the globular cyclohexane molecules between n-alkane molecules and distortion of the hydrogen bond interactions in alkanols by the cyclohexane molecules. Furthermore, the Flory's theory was extended for the theoretical prediction of excess molar volume of these mixtures. The theory predicted the volumetric behavior and magnitudes of excess molar volume satisfactorily.

Anyway, from the above concise literature survey it is obvious that there is a lot of reports on the thermodynamic, acoustic, transport and allied properties for the binary and ternary mixtures consisting of one or more of the liquids studied in the chapters embodied in the present dissertation but reports on the thermodynamics, acoustic and allied properties on the compositions of the various mixtures (binary, ternary and quaternary) studied herein this dissertation are rare to the best of our present knowledge, at least at multi-temperature range.

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