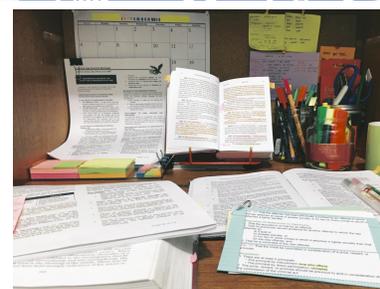
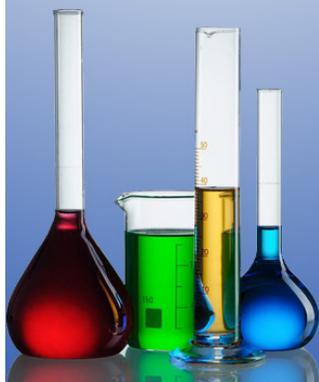




Chapter 1

INTRODUCTION



CHAPTER-1 INTRODUCTION

1.1: Introduction

An investigation in the possible change of thermodynamic properties of binary liquid mixtures and their degree of deviations from ideality has been found to be an excellent qualitative way to elicit information about molecular structure and inter – molecular forces in liquid mixtures.

Thermodynamics is the basis for any experimental science. It is therefore concerned with macroscopic properties of the systems containing many millions of molecules. The thermodynamic properties of liquid mixtures have relevance in understanding the molecular interactions between the components of the mixtures in developing new theoretical models and also in carrying out engineering applications in the processing industry. The ultimate goal of the thermodynamics of liquid mixtures is to predict excess properties from the pure component properties without any experimental knowledge of the actual systems itself. Knowledge about molecular size, molecular structure and polarity allows one to make some qualitative predictions about the behavior of such molecules in liquid mixtures. However, the progress in the field of molecular theory has reached those heights where we can directly predict the properties of a mixture from the nature of its constituents.

To understand the nature of interactions amongst the constituents in a liquid mixture, the non availabilities of thermodynamic data is the main problem. Such types of interactions are involved in the formations of complicated chemical complexes in the binary liquid mixtures and are also responsible for the non – ideal thermodynamic behavior of systems. All these studies of solutions of non-electrolytes are concerned with the evaluation of excess thermodynamic functions. These quantities represent the deviation of the real properties of the mixture from those of an ideal mixture. Examples are given by Scatchard¹, Rowlinson², Douheret, et al.³, Davis and Douheret⁴, Reis, et.al.⁵ and Douheret.et al.⁶⁻⁸ containing some excess differential functions of binary mixtures which exhibit unusual sensitivity to changes in composition. They also developed a concise thermodynamic formalism for the isentropic thermal

expansion, the ideal and excess quantities for the molar and isentropic thermal expansion, and the ideal and excess quantities for the molar and isentropic expansion of binary liquid mixtures. The theoretical values of the excess thermodynamic functions depend critically on the assumption about the depth of their interactions and size. For example, mixtures of molecules of the same size with different depth of interactions have quite different properties from the mixtures of molecules differing mainly in size. However, if there is identical interaction, then differences in masses are responsible for the characteristic deviations from the ideality of the solutions. The extreme sensitivity of the excess functions due to size, shape and interactions provide the important information about the difference in the intermolecular forces which may be obtained from the study of suitable mixtures.

Further, the current theories of solutions and their results which are expressed in terms of excess thermodynamic functions can be successfully checked, if the experimental data for excess functions of suitably selected systems are available. This prompted the researchers to undertake a study to understand these important functions. These thermodynamic excess functions which depend on the composition and temperature of the system are of great importance to the study. Therefore, it is important to have available experimental information of mixtures which can be used as evidence either directly for process design or for the development of empirical correlation or for the improvement of theoretical knowledge.

The increasing use of carbitols and different amines in many industrial processes as well as theoretical interest in the nature of associated solutions have greatly stimulated the need for extensive information on properties of mixtures involving these components. It is interesting to study the thermodynamic, acoustic⁹ and transport properties¹⁰ of non-electrolyte liquid-liquid mixtures, which provide information about the type, extent of molecular interactions and can be used for the development of molecular models for describing the behavior of solutions (Prausnitz, et al.¹¹, Oswal and Patel¹² Oswal, et al.¹³⁻¹⁵).

The study of thermo physical and thermodynamic properties of liquid mixtures is important for the designing of several types of relevant industrial equipment that can provide useful information about the intermolecular interactions in the liquid mixtures, based on experimental measurements. When two liquids are mixed together,

the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to change in free volume, change in free energy, and change in molecular interactions, molecular orientation and steric hindrance. The mixing of different liquid compounds gives rise to solutions that generally do not behave as ideal solutions. Ideal solution is defined in terms of Raoult's law and Dalton's law. A solution which obeys these laws is said to be an ideal solution. For the period of last few years, investigations of thermo physical and thermodynamic properties Marsh and Boxall¹⁶, Heintz¹⁷, Zhang et al¹⁸, Fredlake¹⁹, Tokuda et al.²⁰⁻²², Azevedo et al.^{23,24}, Domanska^{25,26}, Pereiro et al.²⁷, Pereiro and Rodriguez²⁸ and Greaves et.al.²⁹ have increased remarkably but they are by no means exhausted.

Experimental data of thermodynamic and thermo physical properties of liquids and liquid mixtures are fascinating and of high fundamental, practical importance for the industry. Although a qualitative connection between the macroscopic and microscopic features is feasible, quantitative conclusions are of interest to both academic and industrial communities. Thermodynamic and physical properties of liquid mixtures are useful in different ways in terms of their applications, such as

- (i) to find the applicability of theories of liquids and to predict the properties of mixtures,
- (ii) to test the current theories of solutions because of their sensitivity to the difference in magnitude of Intermolecular forces and geometry of the component molecules,
- (iii) to understand the intermolecular interactions between different species of solution,
- (iv). Further, the volumetric properties are useful for designing the industrial plants, pipelines and pumps with better precision,
- (iv) the volumetric studies of liquids mixtures are useful from petro chemistry to pharmaceutical industries,
- (v) the data also finds application in the design of the separation operations such as distillation, extraction, crystallization and so on,
- (vii). the solution effects are also utilized in bio-process development, pollution control and environmental protection.

The properties of mixing and excess properties are provided to be increasingly useful and it is a very challenging area in thermodynamics and many people are being attracted to it. Modern chemical industry, requiring more precise and sophisticated methods of calculation, will be certainly benefited from these developments.

Excess functions³⁰ could be either positive or negative. Their sign and magnitude represent the deviation from ideality. The thermodynamic functions of mixing become identical with thermodynamic excess function in respect of quantities which do not involve entropy.

For an ideal solution all excess functions are zero.

The excess volume (V^E) is given by equation,

$$V^E = V^M_{\text{real}} - V^M_{\text{ideal}} \quad (1.0)$$

Similarly G^E , S^E , H^E , and U^E can be obtained by using the general thermodynamic relation.

Excess Gibbs free energy (G^{*E})

$$G^E = G^M_{\text{real}} - G^M_{\text{ideal}} = RT X_1 \ln \gamma_1 + RT X_2 \ln \gamma_2 \quad (1.1)$$

Where,

$$G^M_{\text{real}} = RT X_1 \ln \gamma_1 + RT X_2 \ln \gamma_2 \quad \text{and}$$

$$G^M_{\text{ideal}} = RT X_1 \ln + RT X_2 \ln$$

Excess Entropy (S^E)

$$\begin{aligned} S^E &= - [\delta G^E / \delta T]_{P, X} \\ &= - RT [X_1 (\delta \ln \gamma_1 / \delta T)_P + X_2 (\delta \ln \gamma_2 / \delta T)_P] - R [X_1 \ln \gamma_1 + X_2 \ln \gamma_2] \end{aligned} \quad (1.2)$$

Excess Enthalpy (H^E)

$$\begin{aligned} H^E &= T^2 [\delta (G^E / T)]_{P, X} \\ &= -RT [X_1 (\delta \ln \gamma_1 / \delta P)_T + X_2 (\delta \ln \gamma_2 / \delta P)_T] \end{aligned} \quad (1.3)$$

Excess volume (V^E)

$$\begin{aligned} V^E &= (\delta (G^E / \delta P))_{T, X} \\ &= RT [X_1 (\delta \ln \gamma_1 / \delta P)_T + X_2 (\delta \ln \gamma_2 / \delta P)_T] \end{aligned} \quad (1.4)$$

Excess internal energy (U^E):

$$U^E = H^E - PV^E - RT[T(X_1(\delta \ln \gamma_1 / \delta T)_P + X_2(\delta \ln \gamma_2 / \delta T)_P)] + P[X_1(\delta \ln \gamma_1 / \delta P)_T + X_2(\delta \ln \gamma_2 / \delta P)_T] \quad (1.5)$$

Where X_1 & X_2 are the mole fractions of components 1 & 2 and γ_1, γ_2 are the activity co-efficient of components 1 & 2. The equations given above involve the activity co-efficient of components of the mixture. The values for activity co-efficient can be obtained from the measurement of vapour-liquid and solid-liquid equilibria. Excess function may be positive or negative and their magnitudes represent the extent of deviation from ideality. The thermodynamic functions of mixing and the excess functions become identical in respect of quantities where in entropy do not appear. For example, the excess enthalpy H^E is identical with the enthalpy of mixing H^E and the excess volume V^E is also identical with the volume of mixing V^E . The thermodynamic functions of mixing are very useful in the study of liquid mixtures. The difference between the values of the function per mole of the mixture and the sum of those per mole of unmixed components at the same condition of temperature and pressure is defined as thermodynamic function of mixing of a binary liquid mixture, and is given by

$$V_m = V - X_1 V_1 - X_2 V_2$$

Where V denotes the molar volume of the mixture, V_1 and V_2 are the molar volumes of the components whose mole fractions are X_1 & X_2 respectively.

1.2 : Historical back ground of study of binary liquid mixtures :

In a Classical sense, the matter has been distinctly divided into three states namely, gas, liquid and solid. Chemists have been curiously working with all the states of matter since the beginning of science. The present thesis is concerned with the liquid state proportions of matter and hence all attempts will be directed to touch only those aspects of chemistry which are relevant to liquid state chemistry.

The most important concept associated with the present understanding of liquids is an idea which originated with the elegant work of Van der Waal around 1887 who suggested that for dense liquids the repulsive forces dominate the liquid

structure. In other words, the shape of molecules determines the intermolecular interactions. Attractive forces like dipole–dipole interactions and other slowly varying interactions also play the same role³¹. The importance of solvent environment in solution is widely appreciated; hence the motivation for the development of the detailed molecular descriptions of liquids and their mixtures is substantial. Thus the area of liquid state chemistry continues to evolve rapidly with realistic descriptions of complex chemical systems. It is becoming increasingly accessible to theoretical analysis. Extensive research over the last few decades in this area alone shows the importance of this study. A number of experimental techniques have been devised and the experimental data have been used to test the theories of mixtures, nevertheless the study of liquid mixtures in chemistry remain an active area of research.

Since 1950, four important monographs covering different aspects of the problem have been published. These are: (a) “Mixtures” by Guggenheim³² which is primarily concerned about the lattice theories of mixtures; (b) “The molecular theory of solutions” by Prigogine³³ which deals about the cell picture of the liquids, average potential model and the corresponding state theories; (c) “liquids and liquid mixtures” by Rowlinson³⁴ which gives an excellent review of the theory and the analysis of experimental data and (d) “Regular solutions” by Hildebrand and Scott³⁵ which discusses various aspects of interactions in real systems.

It is now well established that under special circumstance mixtures of molecules of different size show ideal entropy of mixing. This has been emphasized by striking negative deviations from Roults’s law as found with polymer solutions³⁶. In 1944, Guggenheim³² proposed general theory for the entropy, heat and free energy of mixing for a mixture of molecules containing different number of chain segments of equal size each occupying a site in a quasi-lattice. Later in 1946, Bronsted and Koeford³⁷ published accurate vapour pressure data on a few binary mixtures and observed negative deviations for the free energy of mixing. Since these measurements were done at only one temperature no information was available on the separate contribution of heat and entropy. In 1949, Tompa³⁶ extended Guggenheim’s theory for the energy differences between the end groups and middle groups. In the same year Scatchard and Hildebrand³⁸ have independently suggested the free volume concepts. Also, Hudson³⁹ gave a different concept about mixing of different size

molecules but this was only from the standpoint of packing and density. Meares⁴⁰ tested the ideas of Hudson³⁹ and measured the volume changes on mixing for several esters. He interpreted the observed contraction in terms of geometrical effects. Additionally; he also suggested that for solvents with large molecular differences, their mixtures can pack more closely than either of the pure components.

It is not surprising to note that prior to about 1965 the theory of liquid mixtures was not so well developed. However, largely as a result of the accelerated progress of the theory of pure liquids it is now in a much more satisfactory level of understanding⁴¹. Several different aspects of the problem have been attempted since then. For instance recently, Rossky⁴² has discussed the liquid structure in terms of statistical distribution of relative molecular separations and orientations in the fluid. Models which mimic the real systems have also been suggested.

Computer simulation of liquid structure is another active and promising area of research which has been attempted by a large number of researchers⁴³⁻⁴⁶. These methods provide an exact result for a given model which are rather essential for the testing of analytical theories. In this pursuit, the Monte Carlo method and the molecular dynamic techniques have been widely used⁴². An important feature that is common to most of the simulation techniques is that they require enormous computer time. Computation times in hundreds of hours are needed in many situations. Hence, alternatively attempts have been directed towards the development and testing of analytical theories, which also permit an equally better understanding of liquid state properties.

The exact theory of liquid state and of mixtures has been developed by the methods of statistical mechanics⁴⁷, but the mathematical difficulties involved here are enormous. In addition, several free volume theories have been advanced. In 1950, Kirkwood⁴⁸ showed that free volume theory of Lennard Jones and Devonshire⁴⁹ was only a first approximation for a more exact theory. Salsbury and Kirkwood⁵⁰ have later extended this approach to the study of multi component systems by using the methods of moments in the treatment of order-disorder problem. They have also shown that the retention of first moment gives an approximation of the partition function used by Prigogine³³.

Prigogine and Mathot⁵¹ extended the work of Prigogine and Garikian⁵² by applying the cell model or free concepts to mixtures. They assumed that the molecules are spherical in shape and that the distance of maximum interaction refractive between different types of pairs is approximately the same for these random mixing. Rowlinson⁵³ has made similar observations as feature that the Prigogine and Mathot⁵¹ but the instead made use of the overall quasi-chemical approximation of Guggenheim³² which eliminates into the assumption of random mixing.

In later years, a large number of binary mixtures of hydrocarbon and of nonpolar molecules have been experimented to calculate various excess functions such as excess Gibbs of free energy (G^{*E}), excess volume (V^E) and excess enthalpy (H^E). These are summarized in a review by Swinton⁵⁴. A number studies have been made towards the measurement of excess functions (including excess compressibility's) of mixtures of pseudo spherical molecules of varying degrees of size differences between the mixing species⁵⁵⁻⁵⁸.

A good number of liquid mixtures show deviation from Ideal behaviour. It has become customary to represent quantitatively such deviations from ideal behaviour by means of excess thermodynamic or other physico-chemical functions. The concept of excess thermodynamic properties was first defined by Scatchard in 1931. This is now usually denoted by superscript 'E' attached to the symbol of the appropriate thermodynamic or other functions. The excess thermodynamic properties are most useful in designing of physical separation equipment, developing and proving solution theories and data prediction. Modern chemical industry, requiring more precise and sophisticated methods of calculation will certainly benefit these developments.

The deviation from ideal behaviour is generally attributed to the difference in interactions between like or unlike pair of molecules in the system. The intermolecular forces in liquid mixtures responsible for such interactions are (a) dispersion forces, (b) dipolar forces (non-localized), (c) electrostatic forces (localized) etc.

Dispersion forces are determined by the repulsive and attractive forces between the molecules and the differences in molecular size. The contributions of the repulsive and attractive forces mainly depend on intermolecular distances.

Dipolar forces generally depend upon the permanent dipole moments of the molecules and the relative orientations of these molecules. These also show some dependence on the induced dipole moments of the molecules and intermolecular distances.

Localized electrostatic forces occur between electron deficient molecules and electron rich molecules. The contributions of dispersion and dipolar forces are relatively small, when compared to the electrostatic forces.

1.3: A Brief Review of the Theories of Liquid Mixtures

The aim of any theory of solution is to express the properties of a liquid mixture in terms of the intermolecular forces, which determine these properties. Many theories were formulated (by several people) to account for the deviation of a real solution from the ideal behaviour.

The first systematic attempt to describe the properties of liquid mixtures was made by Van der Waal *et al*⁵⁹ and Van Laar.⁶⁰ In their treatment the Van der Waal's constants 'a' and 'b' of the equations of state were treated as composition.

The deviation from the ideality was attributed to the differences in “Co volume” or “Cohesion” which arise due to the differences in the interactions of the different pairs of molecules present in the solution. This theory was however successful only in explaining deviations in certain excess properties in the critical region of the liquid mixtures. An attempt was made by Dolezalek⁶¹ to account for the non-ideal behaviour of solutions by assuming chemical equilibrium involving either association or salvation or both with all the true molecular species obeying the Raoult's law.

Hildebrand⁶² introduced the concept of regular solution theory. It was used by Scatchard⁵ and formulated the equation for excess volumes.

$$V^E = n K G^E \quad \dots \quad 1.1$$

Where 'n' is the ratio of the internal pressure to the cohesive energy density, assumed to be the same for the pure and mixed components. 'K' is the bulk compressibility which is assumed to be strictly additive in terms of volume fraction. An equivalent equation was derived by Longuet-Higgins⁶³ on the basis of the first order conformal solution theory. The equation is of the form

$$V^E = \frac{\alpha T G^E}{\delta^2} \quad \dots \quad 1.2$$

Where ‘ α ’ is the thermal expansion coefficient. It is assumed to be strictly additive in terms of volume fraction of the components; ‘ δ ’ is the solubility parameter of the mixture and is assumed to be the simple average

$$\delta = \frac{(\delta_A + \delta_B)}{2} \quad \dots \quad 1.3$$

The values of $\frac{\alpha T}{\delta^2}$ and $\frac{V^E}{G^E}$ were compared by Scott⁶⁴ for some mixtures of fluorocarbons with hydrocarbons and it was found that the latter term was greater than the former by about 50% in all cases. Battino and co-workers^{65,66} applied the equation (1.2) to binary mixtures of cyclohexane and carbon tetrachloride and showed that better correlations could be obtained if the values of G^{*E} calculated from regular solution equation were replaced by those obtained experimentally. The drawback of the equation (1.1) is its failure to allow V^E and G^{*E} to have opposite signs in mixtures made up of components (i) which follow the same law of corresponding states and (ii) which have the same intrinsic sizes (i.e. $\overset{\sigma}{A} A = \overset{\sigma}{B} B$).

To the theories of liquids and liquid mixtures two types of approaches are given. The first one considers liquids to be gas like; a liquid is pictured as a dense and highly non-ideal gas whose properties can be described by some equations of state of which Van der Waal is the best known example. The second approach considers a liquid to be solid like, in a quasi crystalline state where the molecules vibrate to and fro about a more or less fixed point in space. The theories based on this concept are called lattice theories. Guggenheim⁶⁷ has formulated and presented the lattice model and it was applied to liquid state by Porter⁶⁸, Hildebrand and Scott⁶⁹. The basic assumptions of this model are that the factorization of the partition function is valid and the internal partition function remains unchanged in the mixture. The free energy of mixing depends only on the configurationally partition function which is given by $Q=Q_{latt} - Q_{vibr}$ where Q_{latt} is the only term that depends on composition and Q_{vibr} is unaffected by mixing. Another assumption is that the lattice is treated as a rigid one i.e. $V^M = V^E = 0$ and each site is occupied by a single molecule. The assumption that $V^E = 0$ was not found valid in case of real solutions. McGlashan and

Morcom⁷⁰ calculated the energies of mixing with zero volume change for pairs of n-alkanes and showed that these agree well with those predicted by the model. However, there is evidence now which shows that TS^E makes a finite contribution to the free energy which was not considered while formulating the theory.

The simple cell model of the liquid state was developed and put forward by Eyring⁷¹. This simple cell model of liquids was used by Lennard-Jones and Devonshire⁷² and Prigogine *et al.*^{73,74}. This approach relates the thermodynamic properties of liquid mixtures to intermolecular energy parameters. The intermolecular energy of a pair of uncharged molecules is given by Lennard-Jones⁷² equation

$$\epsilon = \epsilon^* \left[-2 \left(\frac{\gamma^*}{\gamma} \right)^6 + \left(\frac{\gamma^*}{\gamma} \right)^{12} \right] \quad \dots \quad 1.4$$

Where ‘ ϵ ’ and ‘ γ ’ represent the intermolecular energy and distance of separation respectively. It is assumed that if the Lennard Jones potential is valid for the interaction of A-A and B-B, then it is also valid for the interaction of A-B with the values of ϵ_{AB}^* and γ_{AB}^* given by the following equation.

$$\epsilon_{AB}^* = (\epsilon_{AA}^* \epsilon_{BB}^*)^{1/2} \quad \dots \quad 1.5$$

$$\gamma_{AB}^* = \left(\frac{\gamma_{AA}^* + \gamma_{BB}^*}{2} \right) \quad \dots \quad 1.6$$

An alternate form of equation 1.5 is now used in the study of some liquid mixtures.

$$\epsilon_{AB}^* = l_{AB} (\epsilon_{AA}^* \epsilon_{BB}^*)^{1/2} \quad \dots \quad 1.7$$

Where l_{AB} is an adjustable parameter.

Random mixing of components is assumed by Prigogine and his co-workers who extended this model to mixtures. This assumption was justified by the calculations of Rush Brooke⁷⁵ and of Prigogine and Garikian⁷³. These workers showed that for molecules of the same sizes (i.e. $\bar{A}A = \bar{B}B$), the thermodynamic excess functions are affected only to a small extent due to the deviation from random mixing which occur in real solutions. Prigogine and Mathot⁷⁴ used a smooth potential model in which square-wall potential was substituted for Lennard Jones and Devonshire potential. This approach could explain the opposite signs of the excess free energy and excess volume.

The above theory was later extended by Prigogine and Belleman⁷⁶ to the general case where $\gamma_{AA}^* \neq \gamma_{BB}^*$. It was assumed that cells of two different sizes exist in the liquid mixtures in which cells containing molecules of 'A,' being different in sizes from those containing molecules of 'B'. The ratio of the diameters of the cells is then chosen so as to minimize the free energy of the mixture. It was shown by this work that a large positive excess volume would result from quite a small difference in molecular size. It follows from this that negative excess volume which should occur for mixtures of molecules of the same size would be rarely observed. Discrepancies between the observed and calculated values of excess functions derived from the cell model have been attributed to (a) the failure of the model and/or (b) errors introduced by the assumptions made about the molecular movement and relationship within the mixture. To overcome some of these discrepancies the theories based on corresponding states were developed. The properties of the mixtures and of the pure components are expressed in terms of a reference liquid. The extension of corresponding states theory to mixtures is based on the fundamental assumption that a mixture can be a hypothetical pure liquid whose molecular size and energy are determined by those of its components. This theory makes use of two characteristic parameters ϵ^* , the energy of molecular pair at its equilibrium distance and σ^* , the collision diameter.

Three models were proposed by Scott⁶⁸ for averaging the intermolecular energy parameters for mixtures. These are called “one-liquid,” “two-liquid” and “three-liquid” models. The first two correspond to Prigogine’s ‘crude approximation’ and refined average potential model respectively. In this the calculations are made taking one of the two components as a reference substance and ϵ and σ along with experimental PVT data are used to establish a basic reduced equation of state to fit the pure components and mixtures. According to the first model, the mixture behaves as a single liquid with an effective interaction which is the average of the separate pair interactions. In the “two liquid” model the mixture is regarded as a mixture of the appropriate amounts of a A-centered liquid with parameters (ϵ_A) and $(\sigma)_A$ and a B-centered liquid with parameters (ϵ_B) and $(\sigma)_B$. The ‘three-liquid’ model treats mixture as one that consists of three independent liquids in approximate amounts of pure A, pure B and an imaginary liquid with intermolecular

energy parameters ϵ_{AB} and σ_{AB} . Street and Staveley⁷⁷ examined V^E data of simple mixtures and arrived at the following conclusions.

1. All the three models predict that V^E will be negative if the two components have the same size of the molecules.
2. The calculated values of V^E are more affected by the ratio of σ^* parameters than the ϵ^* parameters.
3. The uncertainties in selecting intermolecular energy parameters can only partly be responsible for the lack of agreement between theory and experiment.
4. The “three-liquid” model predicts a systematic dependence of V^E on mole fraction, while the other two models predict rather asymmetric V^E curves.
5. The disagreement between the theory and the experiment may be due to deviation from combination rules used in formulating the theory.

Bellemans *et al.*^{78,79} thoroughly examined the average potential model and concluded that (i) the model is valuable for predicting the sign of the excess functions of mixtures of roughly spherical molecules, (ii) the corrections that have to be applied to the average interactions, evaluated assuming a random distribution are of the order 5-10% and (iii) a variation of 50% in the excess functions was found in going from 6-12 to 7-14 potential. The two-liquid theory provides a convenient point of deviation for deriving semi-empirical equations to represent thermodynamic excess functions. Such equations were derived by Renon and Prausnitz⁸⁰ with the idea of the local composition to the two-liquid concept.

Prigogine *et al.*,^{73,74} using the cell model as the basis extended the corresponding states approach to chain molecules. A chain molecule is considered as a series of quasi-spherical segments. The interactions of these segments with the neighbouring chain are characterized by the intermolecular energy and separation. The chain is then specified by a number of segments, the external contacts that these make with the other segments and the external degree of freedom. The reduced parameters (volume, energy and entropy) are related to the above specifications of the chain. The law of corresponding states applied to chain molecules met with a noteworthy success.

Balescu⁸¹ extended the Prigogine's average potential model to solutions of molecules of different sizes and dipolar character. An equation for the energy of molecules was established which included both dipolar and induced dipolar forces. In the calculation of dipolar interactions and overall orientations, Balescu used the canonical average taking only the leading terms. Excess functions thus obtained consists of three terms, one being the contribution of central forces while the other two are due to orientational forces of dipolar origin. Rowlinson⁸² pointed out that the Balescu's treatment suffers from faulty averaging of the direct dipole-dipole interaction terms and suggested that the average of the free energy as shown by Onsagar⁸³ and Rush Brooke⁸⁴ would be better for elliptical molecules. Deshpande and Pandya⁸⁵ analyzed the experimental values of V^E of solutions made of two components with permanent dipole moments and found that a modified version of Balescu's approach gave good results. Chand and Ramakrishna⁸⁶ and Naidu⁸⁷ who made use of average potential model along with Balescu's adjustable parameter concluded that Balescu's treatment in its original form is not applicable.

The Bronsted and Koefod's⁸⁸ principle of congruence gives an expression for the activity coefficient of a given component in a liquid mixture of n-alkanes and states that it depends only on the average number of carbon atoms per molecule. Desmyster and Van der Waal⁸⁹ tested the validity of the principle of congruence using the excess volume data of six mixtures of n-alkanes and found that the mixtures obey the principle. Bhattacharya *et al.*,⁹⁰ applied the principle of congruence to $C_6 + C_{16}$ system and showed that the latter approach gives better results than the former.

The theory developed by Flory and co-workers relates the excess properties of the mixture to measurable macroscopic properties of the pure liquid components. In constructing the partition function of the system the basic assumption is made that the intermolecular energy E_o is inversely proportional to the volume. Otherwise, E_o is assumed to depend on the contact surface area of the molecules. The advantage of the Flory's theory is its ability to predict both H^E and V^E with the same interaction parameter X_{AB} . Excess volumes of binary liquid mixtures of non-polar components were examined in the light of Flory theory by Abe and Flory⁹¹ Battino and coworkers⁹², Rastogi et al⁹³ and Benson and co-workers⁹⁴⁻⁹⁷. These workers found that the agreement between the theoretical and experimental values of V^E is good.

Naidu and co-workers⁹⁸⁻¹⁰⁰ studied the applicability of the theory to mixtures that contained one polar component and showed that the theory qualitatively predicts V^E in some cases.

The theories so far discussed attempts to explain non-ideality of solution in terms of physical intermolecular forces. In addition to these forces there are specific forces of new molecular species. These interactions may be expected to occur between molecules having groups with unshared electrons, π electrons and molecules with centres of localised electron deficiency leading to the formation of complexes between the molecules of the components. Mulliken¹⁰¹ designated these complexes as charge transfer complexes. These interactions may be expected to affect the thermodynamic properties to a greater degree as compared to physical interactions.

Hydrogen bond formation between the molecules of a liquid mixture is another common chemical effect that influences the thermodynamic properties of solution to a greater extent than the other specific and physical interactions. Molecules containing hydrogen, linked to an electronegative atom exhibits a tendency to associate with each other and to interact with other molecules possessing accessible electronegative atoms. The extent of self-association and intermolecular bonding between unlike molecules vary with the composition of the mixture (for instance, the dilution of a strong hydrogen bonded liquid by an inert diluents leads to decrease in the concentration of aggregates) with absorption of heat and expansion in volume. The magnitude of positive excess volume will be determined by the structure breaking effect of the inert solvent. If the unlike molecules participate in hydrogen bonding it would result in evolution of heat and contraction in volume. In mixtures wherein both the above effects compete with one another, the sign of excess function will depend on the predominant effect. At present, there appears to be no satisfactory theory of solutions which deal with the strong orientation effects from which one may deduce excess volume. However Flory¹⁰² formulated a theory for associated liquid mixtures. This was employed to deduce equations for excess free energy, excess enthalpy and excess entropy.

The study of liquid mixtures with specific interactions in terms of excess functions is at present utilized for three purposes (i) to study the non ideality of the

mixture (ii) to have an insight into the nature and depth of interactions between unlike molecules, and (iii) to test the theories of binary liquid mixtures.

The excess functions or other properties widely used to investigate the possible interactions in binary liquid mixtures are excess viscosity (η^E), excess molar volume (V^E), excess enthalpy of mixing (H^E), excess Gibbs free energy of activation of viscous flow (G^E), excess magneto rotation (α^E), the interaction term (d^1) of Grunberg and Nissan equation, excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess intermolecular free-length (L_f^E) excess isentropic compressibility (K_s^E) and relative association (R_A) between components etc.

From literature it is evident that the study of the molecular interactions of various organic solvents in aqueous media was reported by many authors. But the study of these molecular interactions of and carbitols [2-(2-methoxy ethoxy) ethanol, 2-(2-ethoxy ethoxy) ethanol and 2-(2-butoxy ethoxy) ethanol] in different amines are scanty. With this view in mind, the thermodynamic study of physico-chemical properties of the binary liquid mixtures of carbitols in different organic solvents of low dielectric constants and high dielectric constants are taken up by the author and the results are incorporated in this thesis in the appropriate chapters.

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