CHAPTER 8
SUMMARY

The thesis deals with studies, principally measurement of excess volume, on the nature and degree of interaction between the components of binary liquid mixtures. Additional evidence in support of the conclusions arrived at in the above investigation is provided by studies on viscosities of these mixtures. The binary mixtures may be classified as follows: (1) Those in which the non-common components do not exhibit self-association due to hydrogen bonding. These consist of toluene and cyclohexane as common components and bromobenzene, nitrobenzene and cyclohexanone as non-common components (2) Those in which the non-common components exhibit self-association due to hydrogen bonding in the pure state. In these mixtures cyclohexane, tetrahydrofuran and cyclohexanone have been used as the common solvents and a group of phenols and a homologous series of aliphatic carboxylic acids as the non-common components. Of the three common solvents, cyclohexane is an inert compound in as much as it does not interact with the second component. The choice of the other two solvents is based on their abilities to interact with the non-common components to different degrees.

The experimental data are reported in detail for each of these mixtures and discussed in terms of the nature and degree of molecular interactions of the components.
A recent theory of interactions of the components of liquid mixtures developed by Flory has been examined using experimental results for excess volume in the case of (1) mixtures of toluene with bromobenzene, nitrobenzene and cyclohexanone (2) mixtures of cyclohexane with nitrobenzene and cyclohexanone. The parameters used for the calculation of $V^E$ are based mainly on interactions between the surfaces of adjoining molecules. The values of $V^E$ experimentally determined are in general agreement with the calculated values. The experimental values have also been explained in terms of loss of dipolar association, $\equiv N - \equiv N$ interactions and formation of charge-transfer complexes.

The excess volumes of binary mixtures of cyclohexane with phenol, o. and p. Chlorophenols and the three isomeric cresols show positive deviations from ideal mixture rule. Since phenols are associated liquids, dilution with cyclohexane may be expected to produce an increase in volume due to progressive decrease in self-association. The effects of substitution on the strength of intermolecular hydrogen bonds in polymers of phenols have also been discussed in terms of the changes in the electron density on oxygen in the -OH group produced by the substituent. In the case of the three isomeric cresols the values of $V^E$ which are greater than that of phenol have been attributed to the inductive effect of methyl group on electron density on the phenolic oxygen. In the case of p-Chlorophenol the
measured $V^E$ has been explained as due to the effect of the substituent group on the electron density at oxygen in the phenolic group through inductive and mesomorphic mechanisms. The value of $V^E$ for cyclohexane - o-Chlorophenol system has been explained as due to (a) presence of intramolecular hydrogen bonds and (b) effect of the substituent on the electron density at oxygen in the phenolic -OH group through inductive and mesomorphic mechanisms.

The data for mixtures of tetrahydrofuran with phenol, o. and p-Chlorophenols and o. and p.Cresols exhibit marked negative deviations from ideal mixture rule. In these mixtures the expansion in volume due to dissociation of self-associated phenols would be counteracted by the contraction in volume produced by hydrogen bond interaction between monomers of phenols and the tetrahydrofuran. The actual result would obviously depend upon the relative magnitudes of the two opposing effects. The experimental results support the conclusion that the hydrogen bond interaction between monomers of the phenols and tetrahydrofuran is stronger than that between two molecules of phenols. The numerical values of $V^E$ of the systems fall in the order: o-Chlorophenol $>$ Phenol $>$ o.Cresol $>$ p.Cresol $>$ p.Chlorophenol. This order has been accounted for by: (a) presence of intramolecular hydrogen bonds in o-Chlorophenol (b) effects of substitution on the polarity of the -OH group in the phenols and (c) concentration of aggregates formed between the unlike molecules.
Data obtained for mixtures of cyclohexanone with phenol, o. and p. Chlorophenols and o. and p. Cresols support the postulates employed to explain the excess volumes of mixtures of tetrahydrofuran with the phenols. The excess volumes of mixtures fall in the order: o-Chlorophenol > phenol > o.Cresol > p.Cresol > p.Chlorophenol. This order is similar to that observed in mixtures of tetrahydrofuran with phenols. This shows that the individual phenols behave in a similar manner in solvents containing donor oxygen atoms. However, the excess volumes of mixtures of tetrahydrofuran with phenols are larger than those of cyclohexanone with phenols. These differences are attributed to differences in basicities and depolymerising abilities of the two solvents.

Acetic acid, propionic acid, n.butyric acid form a homologous series with acid function. These undergo self-association forming cyclic dimers and polymers. Addition of cyclohexane to the acids would be expected to result in expansion in volume due to depolymerisation. The numerical value of $V^E$ is maximum, for an equimolar mixture of cyclohexane and acetic acid. The introduction of one or more methyl groups in the straight chain increases the bond strength between the hydrogen in $-OH$ group and carbonyl oxygen. This leads to: (a) increase in dimerisation and polymerisation in pure state and (b) decrease in depolymerisation on the addition of solvent. The experimental
results are in agreement with these views.

In mixtures of tetrahydrofuran with acetic, propionic and butyric acids, the values of $V^2$ are negative. Tetrahydrofuran unlike cyclohexane has both structure-breaking and structure-making abilities. The experimental results show that the latter effect exceeds that of the former in tetrahydrofuran. The values of $V^2$ are in the order: n-Butyric acid > propionic acid > acetic acid. This order has been attributed to differences in the magnitude of the two opposing effects.

Data for mixtures of cyclohexanone with the three acids are in general agreement with the postulates employed to explain the excess volumes of mixtures of these acids with tetrahydrofuran. However, the numerical values of $V^2$ for the mixtures of tetrahydrofuran with acids are larger than those for mixtures of cyclohexanone with the same acids. These differences support the conclusion that cyclohexanone is a stronger dissociating agent than tetrahydrofuran but a weaker donor.

Viscosities of the binary mixtures have provided evidence for the interactions postulated on the basis of excess volume data. Examination of viscosity data in terms of equations developed by Grunberg and Nissan, and Katti and Chaudhri has shown that the equations are applicable to: (1) mixtures
in which the components are not associated through hydrogen bonding in the pure state, and (2) mixtures in which one component is associated through hydrogen bonding and the other component is non-interacting in nature. Since the values of $\eta$ calculated in terms of Katti and Chaudhri equation which takes into account variation of volume with composition, are close to the values obtained using Grunberg and Nissian equation it is concluded that the former is not superior to the latter. Attempts have been made to correlate deviations in viscosity and excess volumes. It is found in general that the deviations in viscosity, calculated in terms of viscosity relations for ideal solutions proposed by Arrehenius and Reed run antiparallel to excess volumes in sign. It is also found that magnitudes of excess volumes run parallel to deviations in viscosity in mixtures of the homologous series of acids with cyclohexane, tetrahydrofuran and cyclohexanone.

The interactions in the systems studied include dispersion forces, dipolar effects, acid - base interactions and hydrogen bond interactions. These constitute a spectrum of interactions from weak physical interactions to interactions which verge on chemical binding. An attempt has been made to explain the variations in the measured properties on the basis of electronic theory. It is hoped that the present studies will help to give a relatively prominent role for electronic mechanisms as an adjunct to the study of physical and physico - chemical interactions in liquid mixtures.