SUMMARY
Summary

The summary of the work presented in the various parts of this thesis is outlined below.

Since the primary aim of the present work is

(i) to evolve an approach based on the concept of molecular connectivity parameters of the first and third degrees to evaluate $G^E$, $H^E$ and activity coefficients to see as to how it works for binary systems that are characterized by (i) non specific and (ii) weak specific interactions between their components.

(ii) to see if molar excess volumes and molar excess enthalpies of ternary (i+j+k) mixtures of non electrolytes could be evaluated from molar excess volumes and molar excess enthalpies of (i+j), (j+k) and (i+k) binary mixtures.

(iii) to evaluate volume change and enthalpy change along with equilibrium constant for the formation of $1:1$ complex in some binary mixtures; and

(iv) to study $j$-$j$ or $k$-$k$ interactions between the $j^{th}$ or $k^{th}$ components of (i+j+k) mixtures in the presence of the $i^{th}$ component

the entire work has been divided into four chapters:
Chapter - I:

This chapter deals with the role of thermodynamic excess functions in the study of molecular interactions in binary as well as ternary liquid mixtures of non-electrolytes and contains a brief account of intermolecular forces, the sources of their information and the manner of representation of intermolecular potentials. This chapter also includes a brief description of various current theories of solutions of non-electrolytes.

Chapter - II:

This chapter includes a brief review of literature on molar excess volume, $V^E$, molar excess enthalpy $H^E$ and molar excess Gibbs free energy $G^E$ of binary mixtures of non-electrolytes and a brief review of $V^E$ and $H^E$ of ternary mixtures of non-electrolytes.

Chapter - III:

This chapter deals with the purification of chemicals used, checking their purity together with the experimental techniques for measurements of molar excess volumes, molar excess enthalpies of binary and ternary mixtures and Gibbs excess free energies of binary mixtures. The chapter also deals with the NMR and IR studies on binary and ternary mixtures.
Chapter IV

This chapter contains $V^E$ and $H^E$ data at 298.15 K and 308.15 K on

(i) benzene(i) + o-chlorotoluene(j)
(ii) toluene(i) + o-chlorotoluene(j)
(iii) o-xylene(i) + o-chlorotoluene(j)
(iv) m-xylene(i) + o-chlorotoluene(j)
(v) p-xylene(i) + o-chlorotoluene(j)
(vi) 1,4-dioxane(i) + bromoform(j)
(vii) acetone(i) + o-bromoform(j)

$G^E$ data at 308.15 K for

(i) benzene(i) + o-chlorotoluene(j)
(ii) toluene + o-chlorotoluene(j)
(iii) o-xylene(i) + o-chlorotoluene(j)
(iv) m-xylene(i) + o-chlorotoluene(j)
(v) p-xylene(i) + o-chlorotoluene(j)
(vi) 1,4-dioxane(i) + o-chlorotoluene(j)

$V^E$ and $H^E$ data at 298.15 and 308.15 K for

(i) benzene(i) + toluene(j) + o-chlorotoluene(k)
(ii) benzene(i) + o-xylene(j) + o-chlorotoluene(k)
(iii) benzene(i) + p-xylene(j) + o-chlorotoluene(k)
(iv) toluene(i) + o-xylene(j) + o-chlorotoluene(k)

along with the manner of their representation by
Redlick-Kister type equation. This chapter deals with an examination of $V^E$ and $H^E$ data of binary mixtures No. (vi) and (vii) in terms of ideal associated model approach and $V^E$ and $H^E$ data of binary mixtures No. (i) to (v) in terms of

(i) Lacombe and Sanchez theory
(ii) Graph theoretical approach (I)
(iii) Graph theoretical approach (II)

and it has been shown that i-j type of complex is formed between acetone(i) or 1,4-dioxane(i) and bromoform(j) in acetone or 1,4-dioxane(i) according to the reaction $i+j \rightleftharpoons ij$.

The equilibrium constant $K$ and the molar enthalpy of formation ($\Delta H^O$) and change in volume ($\Delta V^O$) have also been calculated for these mixtures using ideal associated model approach.

A graph theoretical approach has also been described for the first time, in this chapter, to evaluate $G^E$ and activity coefficient data for a binary mixture. The versatility of this approach has also been explored in this chapter.

It has also been shown that although the $V^E_{ij}$ and $H^E_{ij}$ values for mixture No. (i) to (v) evaluated from graph theory(I) compare well with their corresponding experimental data, it provides no means to estimate even approximately the activity coefficient data and Gibbs free energy data $G^E$ of binary mixtures of non-electrolytes. On the other hand $Y_i$, $Y_j$, $G^E_{ij}(T,x_i)$ and $H^E_{ij}(T,x_i)$ calculated from the modified graph theory (graph theory II) compare reasonably well with their corresponding experimental values.

It has further been observed that the $V^E_{ij}$ and $H^E_{ij}$ values calculated from graph theory(II) are much more satisfactory than those evaluated by Lacombe and Sanchez theory. The cross
interaction energies $\xi_{ij}^*$ of binary mixtures obtained from an analysis of $H^E$ data in terms of Sanchez and Lacombe theory have also been utilized to see as to how these deviate from geometric mean law, and coupled with the self volume interaction coefficients (predicted from Mayer-McMillen formalism) it has been employed to speculate on the nature of interactions $L$ component of these mixtures.

This chapter also examines the $V^E$ and $H^E$ data of ternary mixtures of non electrolytes in terms of

(i) Lattice theory

(ii) Conformal solution theory

(iii) Sanchez and Lacombe theory; and

(iv) Graph theoretical approach

It has been shown that while both Sanchez and Lacombe theory and "Graph theoretical approach" describe well $H^E_{ijk}$ and $V^E_{ijk}$ data of various ternary mixtures, the quantitative agreement is much better for graph theoretical approach(II) as compared to Lacombe and Sanchez theory. The $V^E$ data of binary and ternary have also been utilized to study the nature of molecular interactions between the $j$th and $k$th components of the $(i+j+k)$ mixture in presence of the $i$th component.
LIST OF PUBLICATIONS

1. Thermodynamic studies of complexation reaction in 1,4-dioxane + bromoform mixture.
   H.P. Dahiya, P.P. Singh and Shashi Dagar,

2. Thermodynamic investigation of complex formation in 1,4-dioxane + bromoform mixture.
   H.P. Dahiya, P.P. Singh and S. Dagar

3. Thermodynamics of molecular interactions in aromatic hydrocarbons + o-chlorotoluene mixtures.
   H.P. Dahiya, P.P. Singh and Shashi Dagar

4. Molar excess volumes and molar excess enthalpies of aromatic hydrocarbons(A) + o-chlorotoluene(B) mixtures at 298.15 K
   Hari P. Dahiya, Shashi Dagar and Prem P. Singh

5. Thermodynamic investigations of molecular complexation in binary acetone + bromoform mixture
   Hari P. Dahiya, Prem P. Singh and Shashi Dagar

6. Molar excess volumes and molar excess enthalpies of some ternary mixtures of non-electrolytes
   P.P. Singh, H.P. Dahiya and Shashi Dagar
7. Thermodynamic and topological investigation of binary mixtures of non-electrolytes; activity coefficient, molar excess Gibbs free energy of mixing and molar excess enthalpies

P.P. Singh, H.P. Dahiya and S. Dagar

8. Thermodynamic investigations of some ternary mixtures of non-electrolytes at 308.15 K

H.P. Dahiya, P.P. Singh and Shashi Dagar