LIST OF PUBLICATIONS

1. Topological aspect of the excess enthalpies of binary mixtures of non-electrolytes.


5. Molar excess enthalpies of ternary mixtures of non-electrolytes.

6. Thermodynamics of binary mixtures.
   P.P. Singh and S.P. Sharma, Fluid Phase Equilibria (communicated).
The summary of the work presented in the various chapter of the thesis is outlined below:

The primary aim of the present work is:

(i) to see if graph theoretical connectivity parameters of pyridine, α-, β- and γ-picolines could be evaluated and the same could be utilized to evaluate molar excess volumes, $V^E$, and molar excess enthalpies, $H^E$, of binary as well as ternary mixtures of non-electrolytes and also to see if the approach could be utilized to evaluate $V^E$ and $H^E$ for an (i+j) mixture at any other temperature;

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

(iii) 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 components.

This was achieved by measuring $V^E$, $H^E$ at 298.15 and 308.15 K for the following binary mixtures:

1. Pyridine (i) + γ-picoline (j)
2. Pyridine (i) + β-picoline (j)
3. Pyridine (i) + γ-picoline (j)
4. Pyridine (i) + cyclohexane (j)
5. γ-Picoline (i) + cyclohexane (j)
6. Methylenebromide (i) + pyridine (j)
(7) Methylene bromide (i) + \( \beta \)-picoline (j) and 
\( V^E \) and \( H^E \) at 298.15 K and 308.15 K of the following ternary 
mixtures:

(i) Methylene bromide (i) + pyridine (j) + \( \beta \)-picoline (k)
(ii) Pyridine (i) + \( \beta \)-picoline (j) + cyclohexane (k)
(iii) Benzene (i) + toluene (j) + 1,2-dichloroethane (k)
(iv) Benzene (i) + o-xylene (j) + 1,2-dichloroethane (k)
(v) Benzene (i) + p-xylene (j) + 1,2-dichloroethane (k)

The entire work is divided into four chapters.

CHAPTER-I introduces the importance of the study of the thermodynamic excess functions to understand molecular inter-
actions in binary as well as ternary mixtures of non-electrolytes and gives a brief account of intermolecular forces, the source of 
their information and the manner of representation of intermolecular potentials. Chapter-I also concerns itself with a brief description 
of the various theories of solutions of non-electrolytes. Some graph theoretical concepts are also defined in this chapter.

CHAPTER-II concerns itself with a fairly comprehensive review of some of the most significant work on \( V^E \), \( H^E \) and 
spectroscopic studies of binary mixtures of non-electrolytes and also of \( V^E \) and \( H^E \) of ternary mixtures of non-electrolytes.

CHAPTER-III confines itself with the purification of materials, checking of their purity and contains a description 
and method of operation of (i) a new dilatometer, (ii) a colori-
meter to measure \( V^E \) and \( H^E \) of binary and ternary mixtures of non-electrolytes. This chapter also contains an 'nmr study of
methylenebromide + β-picoline, β-picoline + pyridine and 1,2-dichloroethane + benzene mixtures.

CHAPTER-IV contains $V^E$ and $H^E$ data at 298.15 and 308.15K of:

i) Pyridine + α-picoline
ii) Pyridine + β-picoline
iii) Pyridine + γ-picoline
iv) Pyridine + cyclohexane
v) β-Picoline + cyclohexane
vi) Methylenebromide + pyridine
vii) Methylenebromide + β-picoline

$V^E$ and $H^E$ data at 298.15 and 308.15 K of:

i) Methylenebromide + pyridine + β-picoline
ii) Pyridine + β-picoline + cyclohexane
iii) Benzene + toluene + 1,2-dichloroethane
iv) Benzene + o-xylene + 1,2-dichloroethane
v) Benzene + p-xylene + 1,2-dichloroethane

and the manner of their representation by Redlick-Kister type equations.

In this chapter a graph theoretical approach has been employed to evaluate $V^E$ and $H^E$ of binary mixtures of non-electrolytes in which at least one component has a hetero atom in its C-C back bone using the graph theoretical connectivity parameters of the third degree and the approach has been shown to be quite successful to describe their $V^E$ and $H^E$ data. The analysis of the $V^E$ and the $H^E$ data of the present (i+j) mixtures in terms of the "graph theoretical" approach has suggested that whereas the packing of i and j in the (i+j) is governed primarily by their C-C skeletal interactions, the
(i+j) interactions in methylenebromide (i) + pyridine (j) and + β-picoline (j) mixtures involve perhaps the valency of individual atoms in their molecular graphs. This chapter also deals with -

(a) an examination of V^E and H^E data of binary mixtures of non-electrolytes in terms of :

i) Flory's theory

ii) Sanchez and Lacombe theory; and it has been shown that the V^E and H^E values predicted by "graph theoretical approach" compare well with the experimental values unlike the V^E and H^E values calculated by Flory's theory or Sanchez and Lacombe theory. It has also been shown that a slightly modified version of the approach proposed originally by Sanchez and Lacombe yields V^E and H^E data that compare reasonably well with the corresponding experimental values. The graph theoretical approach has also been utilized to successfully predict V^E and H^E of a binary mixture at any temperature T_2 when its V^E

and H^E data at T_1 are known.

(b) the V^E and the H^E data on ternary mixtures of non-electrolytes have also been analysed in terms of -

i) Lattice theory

ii) Conformal solution theory

iii) Sanchez and Lacombe theory

iv) "Graph theoretical approach"

and it has been shown that both Sanchez and Lacombe as well as the "graph theoretical approach" describe reasonably well the V^E and H^E data of the various mixtures. The analysis of V_ijk(T_1, x_i, x_j) and the H_ijk(T_1, x_i, x_j) data of the various (i+j+k) mixtures studied here suggests that while
the $H_{ijk}^{E} (T_{1}, x_{i}, x_{j})$ values are determined by interactions that involve primarily the valency of individual atoms in the molecular graphs of i, j and k mixtures, the packing of i, j and k in these mixtures is influenced either by their C-C skeletal interactions or by the valency of individual atoms in their molecular graphs. The $V^{E}$ data on ternary mixtures have also been utilized to extract information about self and cross volume interaction coefficients and these have been utilized to study the nature of molecular interaction between the j th and k th components of the (i+j+k) components in presence of the i th components. This chapter also contains an nmr study of methylenebromide (i) + β-picoline (j), β-piroline(i) + pyridine (j) and 1,2-dichloroethane (i) + benzene (j) mixtures and the same has been utilized to suggest a geometry of the proposed 1:1 molecular complex in these mixtures.