SUMMARY

THERMODYNAMIC INVESTIGATIONS OF BINARY AND TERNARY MIXTURES CONTAINING LOW MOLECULAR WEIGHT SPIECIES

SUMMARY

Thesis has been divided into four chapters

Chapter-I

This chapter confines itself with the importance of excess thermodynamic functions to understand the nature of molecular interactions operating among the constituents of mixtures. This chapter also contains a brief discussion of intermolecular forces, the sources of their information, the manner of representation of intermolecular potentials and some current theories of liquid mixtures. Special emphasis has been given to Graph theory (which involves the topology of the constituents of mixtures), Prigogine-Flory-Patterson (PFP) theory and Sanchez & Lacombe theory of liquid mixtures.

Chapter-II

This chapter deals with review of literature of the significant work on excess molar volumes, V^E, excess molar enthalpies, H^E, excess isentropic compressibilities, excess Gibbs free energy, G^E of binary and V^E, H^E of ternary mixtures. The results of various statistical theories/models on binary and ternary mixtures (components differing in size, shape and polarity) have also been discussed in this chapter.

Chapter-III

The third chapter entitled "Materials and Methods" deals with the purification of liquids used, examination of their purity and the experimental techniques employed for the measurement of excess molar volumes, excess molar enthalpies, speeds of sound and liquid-equilibrium data of the various investigated binary and ternary mixtures.

Chapter-IV

This chapter is divided into two parts

i)   Thermodynamic of binary mixtures

This part contains excess molar volumes, V^E, excess molar enthalpies, H^E, speeds of sound, u and liquid-vapour equilibrium data at 308.15 K of the following binary mixtures:

(i)   1, 3-dioxolane (i) + aniline (j)

(ii)   1, 3-dioxolane (i) + N-methylaniline (j)

(iii)   1, 3-dioxolane (i) + o-toluidine (j)

(iv)   tetrahydropyran (i) + aniline (j)

(v)   tetrahydropyran (i) + N-methylaniline (j)

(vi)   tetrahydropyran (i) + o-toluidine (j)

(vii)   1, 4-dioxane   (i) + aniline (j)

(viii)   1, 4-dioxane   (i) + N-methylaniline (j)

(ix)   1, 4-dioxane   (i) + o-toluidine (j)

and excess molar enthalpies, H^E data of binary

(x)   1, 4-dioxane   (i) + toluene (j)

(xi)   1, 4-dioxane   (i) + p-xylene (j)

(xii)   1, 3-dioxolane (i) + benzene (j)

(xiii)   1, 3-dioxolane (i) + toluene (j)

mixtures measured as a function of composition at 308.15 K.

The observed speeds of sound and liquid-equilibrium data of the investigated mixtures have been employed to predict their isentropic compressibilities, κ_S, excess isentropic compressibilities, κ_S^E and Gibbs free energy, G^E. The observed V^E, H^E, κ_S^E and G^E data of mixtures (i-ix) have been analyzed in terms of (1) Graph theory; (2) PFP theory. The V^E and H^E data of the various binary mixtures (i-ix) have also been analyzed

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in terms of (3) Sanchez & Lacombe theory. Topological and thermodynamic investigations of the studied mixtures have revealed that **D** or **THP** or **D$'$** or **A** or **MA** or **OT** exists as associated molecular entities; (ii) **D** or **THP** or **D$'$** (i) + **A** or **MA** or **OT** (j) mixtures are characterized by interactions between lone pair of electrons on oxygen atoms of **D** or **THP** or **D$'$** and hydrogen atoms of **A** or **MA** or **OT**. The IR studies lend additional support to the nature and extent of interactions for the proposed molecular entities in these mixtures. The V^E, H^E, κ_S^E and G^E values predicted by Graph theory compare well with their corresponding experimental values. Further, PFP theory correctly predicts the sign of V^E, H^E, κ_S^E and G^E values of the investigated mixtures. The V^E and H^E values predicted by Sanchez & Lacombe theory are also of same sign. However, quantitative agreement between experimental and calculated values (by employing PFP and Sanchez & Lacombe theories) is not impressive.

ii)   Thermodynamics of ternary mixtures

This part contains excess molar volumes, V_{ijk}^E and excess molar enthalpies, H_{ijk}^E, data of the following ternary mixtures at 308.15 K.

(i)   1, 4-dioxane (i) + aniline (j) + benzene (k)

(ii)   1, 4-dioxane (i) + aniline (j) + toluene (k)

(iii)   1, 3-dioxolane (i) + aniline (j) + benzene (k)

(iv)   1, 3-dioxolane (i) + aniline (j) + toluene (k)

(v)   1, 4-dioxane (i) + o-toluidine (j) + benzene (k)

(vi)   1, 4-dioxane (i) + o-toluidine (j) + toluene (k)

(vii)   1, 4-dioxane (i) + o-toluidine (j) + m-xylene (k)

(viii)   1, 4-dioxane (i) + o-toluidine (j) + p-xylene (k)

Excess molar volumes, V_{ijk}^E and excess molar enthalpies, H_{ijk}^E data of studied ternary mixtures have been fitted to Redlich-Kister equation to predict ternary adjustable parameters along with standard deviations. The observed V_{ijk}^E and H_{ijk}^E data have been analyzed in terms of (1) Graph; (2) PFP; and (3) Sanchez & Lacombe theories. It has been observed that V_{ijk}^E and H_{ijk}^E data determined by Graph theory compare well their

experimental values. Even in those cases where the calculated and experimental values are not in agreement, they are of same sign and magnitude. The V_{ijk}^E and H_{ijk}^E values, predicted by PFP and Sanchez & Lacombe theories are of same sign {except those of V_{ijk}^E values for $\mathbf{D}'$ (i) + $\mathbf{OT}$ (j) + p-xylene (k) mixture}. However, quantitative agreement between calculated and experimental values is not good.