ABSTRACT

The present dissertation entitled "*Molecular Interactions in Mixtures of Some Industrially Important Solvents: A Physico-Chemical Study*" has been organized in eleven chapters. Chapter I describes the importance of physico-chemical studies on multi-component liquid mixtures with special reference to solvent effects, preferential solvation and various kinds of molecular interactions, *etc.* This chapter also describes the importance and scope of different physico-chemical parameters generally studied for such studies including objectives, applications of the research work and a brief literature review.

Chapter II contains a thorough theoretical background for the research works embodied in this thesis. Chapter III contains details of the chemicals and measurement techniques for different physico-chemical parameters like density, viscosity, ultrasonic speeds of sound, refractive index, *etc.*

Chapter IV describes the thermophysical properties of the binary mixtures of N, N-dimethylformamide (DMF) with some cyclic ethers, *viz.*, tetrahydrofuran (THF), 1,3-dioxolane (1,3-DO) and 1,4-dioxane (1,4-DO) at several temperatures. Excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$) and excess isentropic compressibilities (κ_s^E), *etc.*, were derived from the experimental results. These derived properties were discussed in terms of the nature of component liquids and molecular interactions in the mixtures. The molecular interactions in these binary mixtures were attributed to dipole-dipole and dipole induced dipole interactions. Several empirical and semi-empirical models were used to correlate/predict some of the derived properties.

Chapter V describes the thermophysical properties of the binary mixtures of 2-ethyl-1-hexanol (2-EH) with ethylenediamine (EDA), 1,2-dichloroethane (DCE) and monoethanolamine (MEA) at several temperatures. From the experimental data, various properties like excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$), excess Gibb's free energy of viscous flow (ΔG^{*E}) and different acoustic properties were derived and discussed in terms of molecular interactions like dipole-dipole interaction, hydrogen bond interaction and interstitial accommodation, *etc.* Excess molar volume (V_m^E) and viscosities (η) of the mixtures were correlated with

Prigogine-Flory-Patterson theory, Peng-Robinson Equation of State and Bloomfield-Dewan model, respectively. The results were substantiated with FTIR spectra of these binary mixtures.

Chapter VI describes the molecular interactions of 1,4-dioxane (1,4-DO) with ethylenediamine (EDA), 1,2-dichloroethane (DCE) and monoethanolamine (MEA) at several temperatures. From the experimental physico-chemical properties, several excess or deviation properties (V_m^E, $\Delta\eta$, κ_S^E and R_m^E, *etc.*) were derived and discussed. The study revealed that the degree of molecular interactions follow the order: (1,4-DO + MEA) > (1,4-DO + EDA) > (1,4-DO + DCE). This order of molecular interactions can be ascribed to intermolecular hydrogen bond formation and interstitial accommodation depending on the nature (shape and size) of the mixing components. The nature and extent of molecular interactions were well corroborated with the FTIR spectra of these mixtures.

Chapter VII describes the thermophysical properties of the binary mixtures of cyclohexane (CH) with three esters, *viz.*, methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS) at several temperatures. Experimental densities, viscosities, ultrasonic speeds of sound and refractive indices were utilized to derive various excess or deviation properties (V_m^E, $\Delta\eta$, κ_S^E and R_m^E, *etc.*), which were discussed in terms of the nature of the component liquids and the molecular interactions like breaking of dipolar association or the three dimensional hydrogen bonded network as well as interstitial accommodation, *etc.*, in the mixtures. The order of molecular interactions: (CH + MS) > (CH + EA) > (CH + MA) was well corroborated with FTIR spectra of these binary mixtures. Such an order of molecular interactions manifests a combined effect of several factors like molecular size, shape and nature of the component liquids.

Chapter VIII describes the thermophysical properties of the binary mixtures of cyclohexanone (CHN) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS). From the experimental densities, viscosities, *etc.*, various thermodynamic, transport and acoustic properties were derived and used to explain the molecular interactions in these binary mixtures in the light of breaking up of dipolar interaction, hydrogen bond interaction and interstitial accommodation, *etc.* The order of molecular interactions: (CHN + MS) > (CHN + EA) > (CHN + MA) was

discussed on the basis of the nature of the liquids and the molecular interactions in the mixtures. The above order of molecular interactions was well substantiated by the FTIR spectra of these binary mixtures.

Chapter IX describes the thermophysical properties of the ternary mixtures consisting of cyclohexane (CH) and cyclohexanone (CHN) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS). The experimental densities, viscosities, ultrasonic speeds of sound and refractive indices of seven ternary mixtures and three binary mixtures, *viz*., (MA + EA), (MA + MS) and (EA + MS) were used to derive various excess/deviation properties like V_m^E, $\Delta\eta$, κ_S^E and R_m^E, *etc*. These properties were discussed on the basis of the nature of the mixing components and the molecular interactions in these mixtures. The excess/deviation properties were fitted to Redlich-Kister polynomial (for the binary mixtures) and Cibulka polynomial (for the ternary mixtures). Several empirical/semi-empirical relations like Rastogi, Köhler, Jacob–Fitzner, Colinet, Tsao-Smith, *etc*., were used to correlate/predict the excess or deviation properties of these ternary mixtures. The so-called ternary contributions determined for the ternary mixtures suggested their non-homogeneity.

Chapter X describes the thermophysical properties of two quaternary mixtures consisting of cyclohexane (CH) and cyclohexanone (CHN) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS). The experimental densities, viscosities, ultrasonic speeds of sound and refractive indices were utilized to derive V_m^E, $\Delta\eta$, κ_S^E and R_m^E, *etc*., which helped to reveal the nature of the molecular interactions in these quaternary mixtures. The excess/deviation properties were fitted to Cibulka plymonial for the quaternary mixtures. The study revealed the following order of molecular interactions: (CHN + MA + EA + MA) > (CH + MA + EA + MA) suggesting that the molecular interactions in these quaternary mixtures depend on the nature of the mixing components as well as on the molecular interactions of the associated ternary and binary mixtures at least qualitatively.

Finally in chapter XI concluding remarks on the research works embodied in different chapters (chapters IV to X) of this thesis have been made.