

CHAPTER XI

Concluding Remarks

The present thesis involves the experimental measurements of the densities, viscosities, ultrasonic velocities and refractive indices of binary, ternary and quaternary liquid mixtures. These experimental data helps in the investigation of the nature and molecular interactions amongst the unlike components of the various multi-component liquid mixtures in terms of various derived excess or deviation properties.

In chapter IV thermophysical properties of the binary mixtures of N, N-dimethylformamide (DMF) with tetrahydrofuran (THF), 1,3-dioxolane (1,3-DO) and 1,4-dioxane (1,4-DO) at several temperatures were studied. The nature and magnitude of various excess or deviation properties (V_m^E , $\Delta\eta$ and κ_S^E) suggests the following order of molecular interactions: (DMF + THF) > (DMF + 1,3-DO) > (DMF + 1,4-DO) and the molecular interactions also increase with the increase of temperature. The excess partial molar volumes ($\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$) were found to be negative for all the binary systems except the binary mixture containing 1,4-DO. Also the excess partial molar volumes at infinite dilution ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) were found to be negative for both the components in all the binary mixtures except (DMF + 1,4-DO) mixture. Therefore, while the (DMF + 1,4-DO) mixture is characterised by volume expansion the other two mixtures were characterised by volume contraction. The excess molar volumes of the mixtures were predicted using Prigogine-Flory-Patterson (PFP) and ultrasonic speeds of sound for the studied binary mixtures were also predicted using various empirical and semi-empirical models.

In chapter V the thermophysical properties of the binary mixtures of 2-ethylhexan-1-ol with some 1,2-disubstituted ethanes were studied in terms of various excess or deviation properties. These properties show both positive and negative deviations from ideal ones. An inspection of excess molar volumes, viscosity deviations, isentropic compressibilities, *etc.*, suggests the following order of molecular interactions: (2-EH + MEA) > (2-EH + EDA) > (2-EH + DCE). However, the degree of molecular interactions for each binary systems studied becomes weaker at higher temperatures, probably due to enhanced thermal agitation and kinetic energy

of the component molecules at higher temperatures. The excess partial molar volumes ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) for both the components in the mixtures (2-EH + EDA) and (2-EH + MEA) were negative. However, more negative values of these properties for (2-EH + MEA) mixture than (2-EH + EDA) mixture suggest the following order of packing efficiency or structure compactness in the mixtures: (2-EH + MEA) > (2-EH + EDA) > (2-EH + DCE). The excess molar volumes were correlated using Prigogine-Flory-Patterson (PFP) theory and Peng-Robinson Equation of State (PREOS) based model. The viscosities were correlated using PREOS and Bloomfield-Dewan models. The ultrasonic speeds of sound were also predicted using various empirical and semi-empirical models like Collision factor theory (CFT), Nomoto relation (NOM), Impedance dependence relation (IDR), Ideal mixture relation (IMR) and Junjie (JUN). FTIR spectra of the mixtures also supported the nature of molecular interactions observed for the studied binary systems.

In chapter VI physico-chemical properties of the binary mixtures of 1,4-dioxane (1,4-DO) with ethylenediamine (EDA), 1,2-dichloroethane (DCE) and monoethanolamine (MEA) were studied at several temperatures. Various excess or deviation properties were determined for the experimentally measured densities, viscosities, ultrasonic speeds of sound and refractive indices. These properties were interpreted in terms of dipole-dipole interactions and H-bond interactions amongst the mixing components and the following order of molecular interactions: (1,4-DO + MEA) > (1,4-DO + EDA) > (1,4-DO + DCE) has been found. The degree of molecular interactions however decreases at higher temperatures owing to thermal disruption of developing dispersion forces, non-specific interactions and specific interactions (H-bonding) amongst the liquid components of the mixture. A comparison of the partial molar volume ($\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$) at infinite dilution to molar volume of the respective pure liquids reveal that except the mixture (1,4-DO + MEA), the other two mixtures are characterised by volume expansion. For the studied binary systems Prigogine-Flory-Patterson (PFP) and Peng-Robinson Equation of State (PREOS) were found to predict the excess molar volumes satisfactorily. FTIR spectra of these mixtures showed characteristic band shifts in position and intensities in accordance with the nature of the molecular interaction of the mixtures.

Chapter VII describes the thermophysical properties of the binary mixtures of cyclohexane (CH) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS) at several temperatures. Experimental densities, viscosities ultrasonic speeds of sound and refractive indices were utilised to derive various excess or deviation properties like excess molar volumes, viscosity deviations, excess isentropic compressibilities, excess molar refractions, *etc.* An analysis of these properties revealed the following order of molecular interactions: (CH + MS) > (CH + EA) > (CH + MA). Such an order of molecular interactions originates from a combined effect of several factors like the molecular size, shape and nature of the components; herein the order is attributed to the breaking up of dipolar interactions or the three dimensional hydrogen bonded network as well as interstitial accommodation on mutual mixing of the components. A comparison of the excess partial molar volumes ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) at infinite dilution to the molar volumes of the pure components of the mixtures suggests that while the mixtures with MA and EA are characterized by volume expansion, the mixture with MS is characterized by volume contraction on mixing with CH. FTIR spectra of the mixtures also correlate well with the observed molecular interactions for the mixtures studied.

Chapter VIII describes the thermophysical properties of the binary mixtures of cyclohexanone (CHN) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS) at several temperatures. Various excess or deviation properties determined from the experimental physico-chemical properties like density, viscosity, ultrasonic speed of sound, *etc.*, were interpreted in terms of breaking up of dipolar interactions or three-dimensional hydrogen bonded network as well as interstitial accommodation, *etc.* The study revealed the following order of molecular interactions: (CHN + MS) > (CHN + EA) > (CHN + MA). A comparison of the excess partial molar volumes ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) at infinite dilution to the molar volumes of the pure components of these mixtures suggests that the molecular compactness increases in the same order of molecular interactions as shown above. The Applicability of PFP theory, PR-EOS and Bloomfield-Dewan models were tested for the prediction of V_m^E and η values of the mixtures. FT-IR spectra of the mixtures also correlate well with the observed molecular interactions for the mixtures studied.

Chapter IX describes the thermophysical properties of the ternary mixtures of cyclohexane (CH) and cyclohexanone (CHN) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS) at several temperatures. In this chapter molecular interactions of the binary mixtures between the ester molecules were also studied through the determination of the densities, viscosities, *etc.* Based on the excess or deviation properties like V_m^E , $\Delta\eta$, *etc.*, for the three binary mixtures (MA + EA), (MA + MS) and (EA + MS), the following order of molecular interactions were observed: (MA + MS) > (EA + MS) > (MA + EA). The excess partial molar volumes ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) at infinite dilution of these binary mixtures also support the above order of molecular interactions. Various excess or deviation properties of the studied ternary mixtures (CH + MA + EA), (CH + MA + MS), (CH + EA + MS), (CHN + MA + EA), (CHN + MA + MS), (CHN + EA + MS) and (MA + EA + MS) suggest that these mixtures are characterized by the nature of their mixing components as well as by the nature of molecular interactions in the associated binary mixtures. These excess or deviation properties of the ternary mixtures were fitted to Cibulka equation and the so-called ternary contributions ($X_{m,123}^E - X_{Bin}^E$) were derived; although these contributions are rather small but their maximum and minimum values suggest non-homogeneity in these ternary mixtures and the binary contributions (X_{Bin}^E) play a significant role in characterizing the ternary mixtures studied. Further the empirical models like Köhler, Jacob–Fitzner, Colinet, Tsao–Smith, Toop, *etc.*, were tested to estimate theoretically the excess molar volumes, viscosity deviations, *etc.*, and these models were found to be suitable for the studied ternaries.

Chapter X describes the thermophysical properties for the quaternary mixtures of cyclohexane (CH) and cyclohexanone (CHN) with methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS) at several temperatures. The various excess or deviation properties like excess molar volumes, viscosity deviations, *etc.*, derived for these quaternary mixtures revealed the following order of molecular interactions: (CHN + MA + EA + MS) > (CH + MA + EA + MS). This order of molecular interactions suggests that these mixtures are characterised by the nature of the component liquids as well as by the molecular interactions prevailing in the associated binary and ternary mixtures. Various excess or deviation properties of these mixtures

were also correlated with two symmetric models given by Köhler and Jacob–Fitzner. Both these models were found to correlate the excess or deviation properties satisfactorily.

In summary the physico-chemical study of multi-component liquid mixtures provide valuable information about the extent and nature of molecular interactions (amongst the component liquids) that ultimately predicts the overall structure of such mixtures in the liquid state. Information on the molecular interactions often helps to develop new theoretical models, which aid to have valuable academic information on various physico-chemical properties of the related mixtures; because it is often difficult to understand, explore and interpret molecular interactions in multi-component liquid mixtures. Information on the physico-chemical properties and the liquid structure of multi-component liquid mixtures are actually very much important for their industrial applications. Therefore, studies on physico-chemical properties of such mixtures can prove handy for their selections in process industries. Therefore, physico-chemical studies on multi-component liquid mixtures are never ending as well as worthy of extensive studies.