CHAPTER VI

SUMMARY AND PUBLICATION RECORD

VI.A. SUMMARY

Studies on molecular interactions in liquids and liquid mixtures and their physical properties continue to be pursued with great interest in view of their widespread importance in several areas of applied and theoretical research in addition to their applications in engineering and chemical design processes. Several empirical methods have been developed and used to study the excess thermodynamic properties of liquid mixtures and numerous experimental results have been published in various research journals related to the subject matter. While some of these theories are not satisfactory, others require further investigations. A comprehensive understanding of the liquid state properties of binary organic mixtures comprising liquid components of varying nature such as nonpolar, polar, etc., is not an easy task. However, such a study helps to gain an insight into the thermodynamic behaviour of the mixing process and consequently, to understand the nature of interactive forces between the mixing components.

The present thesis deals with the theoretical and experimental studies on binary organic liquid mixtures. The basic liquid state properties such as density, viscosity, refractive index and speed of sound are determined experimentally at various temperatures and over the whole
range of mixture compositions. These properties are used to calculate the excess quantities that indicate the extent of deviation of mixtures from ideality. Hydrogen bonding, dipole-dipole and dipole-induced dipole, non-specific and non-directional intermolecular interactions are found to be operative depending on the nature of the liquid components. This thesis aims at the evaluation of excess thermodynamic, acoustic, hydrodynamic and optical properties of 41 binary mixtures from the measured physical properties such as density, viscosity, refractive index and speed of sound to gain a better understanding of the type and nature of interactions. The problem of the thesis is divided into six chapters.

From the basic physical properties of liquids and their mixtures, excess molar volume $V^E$, deviations in viscosity $\Delta \eta$, deviations in molar refractivity $\Delta R$, deviations in speed of sound $\Delta u$, and deviations in isentropic compressibility $\Delta k_s$, have been calculated. Such an approach would provide a considerable amount of factual knowledge about the type and nature of interactions in liquid mixtures. These properties are fundamentally useful in making the important decisions about the suitability of a liquid mixture in practical applications such as liquid-liquid distillation, separation, miscibility, solubility, etc. Additionally, from a fundamental viewpoint, the derived parameters will add further to the existing knowledge about the molecular interactions between components of the mixtures and thereby help to predict the mixing behaviour of liquids.
Forty one binary organic mixtures have been chosen for this study depending on the type of the intermolecular forces such as dispersion forces, dipole-dipole interactions, hydrogen-bond effects, etc. Of these, ten mixtures comprise of aqueous-organic systems. The dispersion type forces due to non-specific and non-directed interactions have been interpreted in terms of the positive value of $V^E$. However, the existence of other specific interactions have been discussed and interpreted in terms of the negative $V^E$ results. Empirical fittings treating both temperature and composition effects on density, viscosity, refractive index and speed of sound of the mixtures have been attempted. A discussion is made on the validity of the refractive index mixing rules to predict the deviations in molar refraction of the mixtures.

The first chapter of the thesis covers an up-to-date survey of the literature on the study of organic binary liquid mixtures and their properties. Only useful and relevant papers are cited. An attempt has been made to cover the latest developments and discussion of the published literature data on excess volume, deviations in speed of sound, isentropic compressibility, viscosity and refractive index. In the literature, the other useful properties of the mixtures studied are excess enthalpy and excess free energy of mixing. However, both the experimental and theoretical aspects of liquids and liquid mixtures are covered in this chapter.

In the second chapter, experimental and computational details are given. A description of the solvents used and reasons for the selection of these solvents is followed by
details about the apparatus and instruments used. Experimental procedures for the determination of density, viscosity, refractive index and speed of sound are outlined. A double-arm pyknometer (Lurex, 10 ml capacity) is used to measure density, while Cannon-Fenske viscometers (sizes 75, 100 and 150) are used to determine the flow time of liquids and their mixtures. Refractive index has been measured by using an Abbe Refractometer (Bellingham and Stanley Ltd., London) while the speed of sound is measured using a multifrequency interferometer, model M-84, supplied by Mittal Enterprises, New Delhi. A single-pan Mettler balance (model AE-240, Switzerland) is used throughout the research for mass determinations. The temperature range for measurement of all physical properties is fixed between 298.15 and 318.15 K. Details about computations of mixing functions and regression analysis are given.

The third chapter is divided into three sections. In the first section, experimental results on density, viscosity, speed of sound and refractive index of the binary mixtures of diglyme with ethyl acetate, methyl benzoate, ethyl benzoate and diethyl succinate are given. These results are used to test the validity of the refractive index mixing rules and viscosity equations. Excess molar volume, excess free volume of mixing, deviations in molar refractivity and speed of sound are calculated. In addition, other thermodynamic quantities such as excess isentropic compressibility, excess isothermal compressibility and isobaric thermal expansivity of the mixtures have been calculated.
It is observed that mixtures of diglyme with aromatic esters such as methyl benzoate and ethyl benzoate exhibit large volume contractions. In case of mixtures of diglyme with aliphatic esters viz., ethyl acetate and diethyl succinate, volume contractions are comparatively smaller. Negative $V^E$ in these mixtures is attributed to weak dipole-induced dipole as well as dipole-dipole type interactions.

The effect of temperature on excess molar volume is studied for mixtures of diglyme with ethyl acetate and methyl benzoate as a typical example of aliphatic and aromatic ester. It is observed that with increasing temperature, specific interactions arising from induced dipole-dipole type interactions also increase. This increase is more with aliphatic esters than with the aromatic esters.

In case of diglyme + methyl benzoate mixtures, a large negative $\Delta k_s$ is observed, whereas for diglyme + ethyl acetate mixtures, these values are less negative and also the dependence is not uniform. However, in case of mixtures of diglyme with diethyl succinate or ethyl benzoate, the $\Delta k_s$ values show the sigmoidal trends and exhibit both positive and negative values.

An interesting observation is seen when diglyme + diethyl succinate mixture was placed in the ultrasonic cell at a frequency of 1 MHz and the experiment continued. At 308.15K, the colour of the mixture turned light blue. At temperature of 318.15K, the solution turned dark blue which remained
permanent even after keeping the mixtures for nearly sixty days. Possibly because of this anomaly, the behaviour of \( \Delta k_s \) versus \( \phi_1 \) curves for this mixture are different from the usual observations. Also, in case of diglyme + ethyl benzoate mixtures, another unusual effect is observed. At temperatures above 298.15K, the solution turned green with the formation of an emulsion at a frequency of 4 MHz. This mixture also exhibited an unusual sigmoidal shape for the dependence of \( \Delta k_s \) on \( \phi_1 \) at 298.15K. A plausible explanation for these effects is the formation of a molecular complex under the influence of sonic waves. A systematic trend in the decrease of \( \Delta k_s \) values with an increase in temperature is observed for all mixtures.

From the speed of sound and density results, the specific acoustic impedance factor \( z \), is calculated. It is realized that the molecules which have the ability for specific intermolecular interactions such as diglyme and esters exhibit high \( z \) values. The calculated values of \( z \) at 298.15K for diglyme and methyl benzoate are respectively, \( 1.559 \times 10^6 \text{ kg.m}^{-2}\text{.s}^{-1} \) and \( 2.148 \times 10^6 \text{ kg.m}^{-2}\text{.s}^{-1} \), while the value of \( z \) for diethyl succinate at 318.15K is \( 1.564 \times 10^6 \text{ kg.m}^{-2}\text{.s}^{-1} \), which is close to that of sea water for which \( z = 1.57 \times 10^6 \text{ kg.m}^{-2}\text{.s}^{-1} \) at 298.15K. Thus, diglyme at 298.15K and diethyl succinate at 318.15K may serve to be possible candidates as sonar transducer fill-fluids in under-water research.

It is found that for diglyme + methyl benzoate mixtures, \( \Delta R \) exhibits a maximum of \( 0.198 \text{ cm}^3\text{.mol}^{-1} \). This implies that there is a greater molecular orbital perturbation during
mixing of these liquids. However, in case of mixtures of diglyme with ethyl benzoate or diethyl succinate, the variation of $\Delta R$ with $\phi_1$ is almost identical throughout the composition scale. For the latter mixture, $\Delta R$ values are slightly higher at higher composition of diglyme in the mixture. On the other hand, for diglyme + ethyl acetate mixtures, the values of $\Delta R$ are negative. While the effect of temperature on $\Delta R$ is not very systematic for all systems, the mixtures of diglyme + ethyl benzoate, or + diethyl succinate show a significant decrease in $\Delta R$ with increasing temperature.

The $\Delta \eta$ values for all mixtures except diglyme + ethyl acetate are negative over the whole range of mixture composition and at all temperatures. In case of diglyme + ethyl acetate, the values of $\Delta \eta$ show the sigmoidal behaviour. These data for different components of the mixtures vary in the sequence: ethyl benzoate < diethyl succinate < methyl benzoate < ethyl acetate. Effect of temperature on $\Delta \eta$ is not the same for all mixtures. Values of $\Delta \eta$ decrease with an increase in temperature for diglyme + methyl benzoate. However, for the remaining mixtures, $\Delta \eta$ values tend to increase with temperature. The increase in $\Delta \eta$ values for the temperature interval of this study is higher for diglyme + diethyl succinate mixtures than for diglyme + ethyl acetate and diglyme + methyl benzoate. The temperature dependence of $\Delta \eta$ for diglyme + ethyl benzoate mixtures depends on the composition of diglyme in the mixture. Around $x_1=0.2$, the $\Delta \eta$ dependence on temperature reverses suggesting the presence of iso-viscous point at which the hydrodynamic behaviour of the mixtures remains identical for all the temperatures. Such
mixtures may be useful in some specific engineering applications.

Validity of several refractive index mixing rules have been tested and the results of this analysis are given along with the average deviations of the difference (%Δn) between the experimental and calculated refractive indices. Each of the refractive index mixing equations reproduce the measured values within the limits of the experimental precision. Isobaric thermal expansion coefficient α, of the mixtures is obtained from the temperature-dependent density results. One can also calculate α from the temperature-dependent refractive index results using the refractive index mixing rules. From these results, the isobaric thermal expansivities of pure solvents have been determined by differentiating the Eykman and Lorentz-Lorenz relations with respect to temperature. It is observed that the α values thus calculated are in agreement with those obtained from the density results.

Among the viscosity equations, the McAllister, Heric and Auslaender relations are used to test the viscosity results. In addition, a polynomial relation is also used. It is found that McAllister as well as Heric equations fit the experimental viscosities better than the other equations.

In addition to the four binary mixtures discussed above, the previously published experimental results on mixtures of diglyme with methyl acetate, n-butyl acetate and methyl salicylate have also been included in the discussion. The free volume $V_f$ of the binary mixtures have been calculated.
using Eyring and Kincaid relation. The calculated excess free volumes $V_f^E$ are negative for all mixtures of diglyme with esters. The largest negative $V_f^E$ is observed in case of diglyme + ethyl acetate mixtures and the negative $V_f^E$ values for diglyme mixtures containing the esters become less negative. The negative $V_f^E$ values vary according to the sequence: ethyl acetate < methyl acetate < methyl salicylate < methyl benzoate < ethyl benzoate < n-butyl acetate. Excess internal pressure $P_i^E$, has been calculated for the binary mixtures of diglyme with esters. It is found that $P_i^E$ is positive for diglyme + ethyl benzoate, while for the remaining mixtures, it is negative. However, in case of diglyme + n-butyl acetate mixtures, a sigmoidal behaviour is observed. The values of $P_i^E$ are positive at low diglyme content of the mixture; at higher concentrations of diglyme, $P_i^E$ becomes more negative. For all mixtures, the $P_i^E$ values vary in the sequence: ethyl acetate < methyl acetate < methyl salicylate < methyl benzoate < diethyl succinate < n-butyl acetate < ethyl benzoate. Such negative values of $P_i^E$ qualitatively indicate that the repulsive forces are greater than those of the attractive forces. On the other hand, positive values of $P_i^E$ imply that the forces of attraction are greater than those of repulsion.

From an experimental consideration, excess isothermal compressibility $\Delta k_T$ for binary organic mixtures have also been calculated. Mixtures of diglyme with methyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate and methyl salicylate exhibit negative values of $\Delta k_T$ whereas, diglyme + n-butyl acetate mixtures show sigmoidal behaviour and these
values vary from negative to positive. The results of $\bar{V}_1 - V_1$ and $\bar{V}_2 - V_2$ versus mole fraction are presented graphically.

In the second section of the third chapter, binary mixtures of diglyme with alkanes (hexane to hexadecane), 2,2,4-trimethylpentane, cyclohexane and 1,2,3,4-tetrahydronaphthalene are studied. In all these mixtures, excess molar volumes are positive suggesting the weak dispersion-type intermolecular interactions. All the mixtures exhibit negative $\Delta \eta$ and $\Delta u$ values, but the $\Delta R$ values are negative except diglyme + 1,2,3,4-tetrahydronaphthalene mixtures. On the other hand, the $\Delta k_s$ values are positive for all mixtures from nonane to hexadecane.

A systematic dependence of excess volume and deviations in viscosity, refractive index and speed of sound on the chain length of $n$-alkanes is observed, but there is no systematic dependence of $\Delta k_s$ on the alkane chain length. The results of $V^E$, $\Delta \eta$, $\Delta u$ and $\Delta k_s$ show a systematic deviations with increasing temperature. In the third section, the variation of these properties with mole fraction has been studied for mixtures of diglyme with 1-propanol, 1-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol. The effect of temperature on $\Delta \eta$ values are systematic but, the $\Delta R$ values are not greatly affected within the investigated temperature interval of 298.15 - 318.15K.

In the fourth chapter, the results of density, viscosity, refractive index and speed of sound in binary mixtures of water with N,N-dimethylformamide, dimethyl sulfoxide,
N,N-dimethylacetamide, acetonitrile, ethylene glycol, diethylene glycol, 1,4-dioxane, tetrahydrofuran, 2-methoxyethanol and 2-ethoxyethanol are presented at 298.15K. From these results, the excess quantities are computed and these results are analyzed in terms of the intermolecular interactions. The negative $V^E$ results of these mixtures follow the sequence: N,N-dimethylacetamide $<$ N,N-dimethylformamide $<$ 2-ethoxyethanol $<$ 2-methoxyethanol $<$ dimethyl sulfoxide $<$ tetrahydrofuran $<$ 1,4-dioxane $<$ diethylene glycol $<$ acetonitrile $<$ ethylene glycol. However, in all cases, the minima of the curves tend to shift toward the water-rich region of the mixtures.

The values of $\Delta \eta$ are positive for all mixtures except for few compositions in case of mixtures of water with ethylene glycol, diethylene glycol and acetonitrile. The results of $\Delta u$ versus $x_1$ are positive for all mixtures except those of water with tetrahydrofuran, acetonitrile and 1,4-dioxane. However, the results of $\Delta R$ and $\Delta k$ versus $\phi_1$ are negative for all the aqueous-organic mixtures. The variations in $\Delta \eta$, $\Delta u$, $\Delta k$ and $\Delta R$ with mixture compositions support the variations observed in the $V^E$ values of the binary mixtures. Moreover, the $V^E$ results are consistent with the available published data.

The fifth chapter is divided into two sections. In the first section, experimental results for the binary mixtures of 2-ethoxyethanol with $n$-alkanes (hexane to dodecane), cyclohexane and 2,2,4-trimethylpentane are presented, while the second section deals with a study of the binary mixtures of 2-ethoxyethanol with higher alcohols viz., 1-propanol,
2-propanol and 1-butanol. The values of excess parameters are fitted to Redlich-Kister polynomial equation. The basic physical properties are also analyzed simultaneously with mixture composition and temperature by fitting to an empirical equation.

In all the alkane-containing mixtures, the values of $V^E$ are positive and increase systematically with increasing chain length of alkanes from hexane to dodecane. However, the $V^E$ versus $x_1$ curve for cyclohexane is in between those of the curves obtained for octane or nonane mixtures with 2-ethoxyethanol. Similarly, the curves for 2,2,4-trimethylpentane is in between those exhibited by mixtures of hexane and heptane with 2-ethoxyethanol. The positive values of $V^E$ are attributed to the decrease in dipole-dipole interactions between the mixing molecules. The observed maxima in $V^E$ versus $x_1$ curves tend to shift slightly toward 2-ethoxyethanol-rich region of the mixtures from hexane to dodecane.

The deviations in viscosity, molar refractivity and speed of sound at 298.15K for all the binary mixtures are negative and show a systematic variation with increase in the length of $n$-alkanes. Deviations in isentropic compressibility versus volume fraction are sigmoidal for all the mixtures except cyclohexane, decane and dodecane. In mixtures of 2-ethoxyethanol with 2,2,4-trimethylpentane, hexane, heptane and octane, the variation of $\Delta k_s$ with $\phi_1$ shows sign inversions. With mixtures containing nonane, decane and dodecane, the values of $\Delta k_s$ are positive over the entire
composition and the curves are somewhat skewed when compared to the curves for lower n-alkanes.

The sigmoidal shapes observed in mixtures of 2-ethoxyethanol with lower n-alkanes (2,2,4-trimethylpentane, hexane, heptane and octane) result from a shifting of imbalance between relatively large positive contribution due to breaking of the hydrogen-bond structure and a negative contribution from the interstitial accommodation of n-alkane molecules into 2-ethoxyethanol. On the other hand, the interstitial accommodation of n-alkanes into 2-ethoxyethanol multimer structure becomes less effective when the size of n-alkane is large and the positive contribution from the breaking of hydrogen-bonds becomes more predominant giving positive $\Delta k_s$ values over the entire volume fraction range for these mixtures. In the present work, while the effect of temperature on $V^E$ and $\Delta \eta$ values are systematic but, the $\Delta R$ values are not greatly affected within the investigated temperature interval of 298.15-313.15K.

In case of 2-ethoxyethanol + alcohol mixtures, the $V^E$ results for mixtures of 2-ethoxyethanol with 1-propanol, 2-propanol and 1-butanol at 298.15K are small and negative. The curves for these mixtures are somewhat skewed toward the lower concentrations of 2-ethoxyethanol in the mixtures. However, the $V^E$ values of these mixtures increase with the size of alcohol viz., from 1-propanol to 1-butanol suggesting a decrease in specific interactions with increasing size of alcohol. The dependence of $\Delta \eta$ on $x_1$ and $\Delta R$ on $\phi_1$ for all the mixtures are negative.
In the sixth chapter, a summary of the research is presented. The problems encountered during the course of the research and the possible future studies on other aspects of liquid mixture properties are discussed.

In conclusion, the present thesis is a continuing effort in the laboratory of Aminabhavi on the accumulation of binary mixture property data of organic liquids. The results obtained here are worthy of contribution to the advancement of knowledge in the study of binary organic liquid mixtures. The selected binary mixtures have not been studied in the earlier literature and hence are being investigated. Several research articles have been prepared while investigating the present thesis problem. The publication record covers this list.

VI.B. FUTURE POSSIBLE STUDIES

From the knowledge gained in investigating the present thesis problem, it appears necessary to use more experimental techniques to arrive at a comprehensive understanding of the binary interactions such as hydrogen-bond effects, dipolar interactions and other dispersion forces. In this pursuit, Fourier Transform Infrared (FTIR) technique may be useful to study the hydrogen-bond type interactions. An effort in this direction is underway. Similarly, Nuclear Magnetic Resonance (NMR) studies in terms of chemical shifts would provide valuable information.

On the other aspects, in view of the importance of the environmental pollution problems due to the presence of
volatile organic chemicals (VOCs), it is important to investigate the vapour-liquid equilibrium properties of the liquid mixtures, particularly, in case of aqueous-organic mixtures. From such data, one would be able to calculate the excess Gibbs free energy of mixing. On the theoretical side, the evaluation of excess Gibbs free energy of mixing is very important to predict the behaviour of mixture properties. However, it is also possible to evaluate the Henry's law constants for volatile organic chemicals through gas chromatographic techniques in conjunction with the fugacity or activity data of solvents. Also of importance is the study of excess enthalpy of mixtures. In this direction, microcalorimetric investigations are necessary. Use of these methods in our future research efforts will have an improved impact on the understanding of the binary organic mixture properties.

VI.C. PUBLICATION RECORD


[7] Aminabhavi, T.M., Bindu, G., Densities, Viscosities and Refractive Indices of Bis(2-methoxyethyl) ether + Cyclohexane, + 1,2,3,4-Tetrahydronaphthalene and
