Chapter

9

Summary of the investigation and future scope

Contents

9.1 Summary

In the present thesis examines and reports on the dielectric, ultrasonic, volumetric, and refractometric properties of selected systems across different temperatures, along with the validation of mixing models for these systems.

I. Binary mixtures of n-Hexanol + N, N-Dimethylformamide (DMF)
II. Binary mixtures of n-Octanol + N, N-Dimethylformamide (DMF)

This study investigates dielectric relaxation processes, molecular interactions at the atomic level, and their contribution to the dielectric/electrical, ultrasonic, volumetric, and refractometric properties of the systems. It enhances the understanding of the underlying physical mechanisms, ionic conductivity, and dielectric relaxation behavior in solutions of DMF in different solvents (n-Hexanol and n-Octanol). Overall summery of the findings of the present investigation is given bellow;

Chapter 1 outlines the fundamental principles of dielectric, physico-chemical, and acoustic studies of binary liquid mixtures, focusing on selected compounds such as n-Hexanol, n-Octanol, and DMF. It also discusses the properties and applications of these compounds, along with a review of relevant literature to support the investigation. This chapter sets the foundation for understanding the behavior of these systems and their significance in various chemical industries and pharmaceutical applications. ***Chapter 2*** provides a detailed exploration of dielectric theory, focusing on the fundamental concepts of dipole moments, polarization mechanisms, and dielectric relaxation processes. It examines both static and dynamic permittivity models, including Debye, Onsager, Kirkwood, and Frohlich theories for static permittivity, and Havriliak-Negami, Cole-Cole, Debye, and Cole-Davidson models for dynamic permittivity. The relationship between dielectric parameters and molecular behavior is emphasized, particularly in relation to thermodynamic and physico-chemical properties such as ultrasonic velocity, density, refractive index, and viscosity. These connections underscore the role of molecular interactions in governing dielectric behavior. Additionally, the chapter provides an overview of electrochemical impedance spectroscopy, detailing its application in measuring and analyzing dielectric and electrical properties of materials. This comprehensive discussion of dielectric theory and related techniques forms a critical foundation for understanding the complex behavior of dielectric materials in various scientific and industrial applications. ***Chapter 3*** elaborates on the experimental setup and methodologies used for analyzing dielectric properties. Techniques such as low-frequency dielectric relaxation studies, acoustic, refractometric and volumetric measurements and Fourier-transform infrared spectroscopy (FTIR) are described in detail. The chapter outlines the stepwise procedure for preparing binary mixtures, measuring properties like refractive index, viscosity, and density across varying temperatures, and interpreting dielectric spectra. The importance of data validation through empirical and semi-empirical models is also emphasized. ***Chapter 4*** investigates the dielectric relaxation spectroscopy (DRS) properties of binary mixtures, presenting data on dielectric constants, dipolar interactions, and relaxation times, with a focus on temperature-dependent variations. The analysis delves into the effects of molecular structure, hydrogen bonding, and dipole alignment on the dielectric behavior of the mixtures. The chapter assesses the applicability of theoretical models to the experimental data, providing insights into solute-solvent interactions and structural changes. The study examines the concentration-dependent dielectric and electrical properties of n-Hexanol, N, N-Dimethylformamide (DMF), and their binary mixtures across a frequency range of 20 Hz to 2 MHz at temperatures of 293.15 K, 303.15 K, and 313.15 K. At low frequencies, the dielectric behavior is primarily influenced by ionic conduction and electrode polarization, with concentration-dependent shifts observed in the loss tangent and complex permittivity. Experimental data are successfully modeled using the Cole-Cole framework, exhibiting Debye-type relaxation, with relaxation times, such as electrode polarization and ionic relaxation times, showing good agreement with experimental results. Complex impedance and modulus spectra reveal the dominant role of electrode polarization and ionic relaxation processes. The analysis of dielectric parameters, including static and high-frequency dielectric constants, relaxation times, and excess dielectric properties, highlights significant molecular interactions, particularly hydrogen bonding. Nonlinear variations in dielectric constants and relaxation times with increasing mole fraction of n-Hexanol indicate pronounced intermolecular interactions. Thermodynamic parameters, such as activation energy, enthalpy, and entropy of activation, are calculated, offering valuable insights into the energy and thermodynamic characteristics of the mixtures. Additionally, microwave heating parameters reflected power, transmitted power, and penetration depth are evaluated, providing a thorough understanding of the energy dynamics and efficiency of the binary mixtures. ***Chapter 5*** investigates the dielectric and electrical properties of binary mixtures of n-Octanol and DMF across a frequency range of 20 Hz to 2 MHz at temperatures from 293.15 K to 313.15 K. The study reveals that the low-frequency dielectric behavior is dominated by ionic conduction and electrode polarization, with strong concentration dependence observed in both electrode polarization relaxation time and ionic conductivity relaxation time. Experimental complex permittivity data are well-described by the Cole-Cole model, with calculated relaxation times (τ_{EP}, $\tau_{EP'}$, τ_{σ}) showing good agreement. The dispersion observed in the M' spectra and Z" versus Z' plots highlights the separation of bulk and electrode surface effects, with impedance data fitting to a three-element RC equivalent circuit confirming various electrical processes in the sample and at the electrode surface. The scaling of tan δ and M" with concentration variation suggests the potential for tuning the electrical and dielectric properties of n-Octanol by mixing with DMF. In the microwave frequency range (200 MHz to 20 GHz), the complex permittivity spectra of the binary mixtures also fit well to the Cole-Cole model, revealing a decrease in dielectric strength ($\Delta\varepsilon$) with increasing n-Octanol concentration, suggesting weaker intermolecular interactions due to reduced dipole-dipole interactions. Negative values of excess static permittivity and excess inverse relaxation time at most concentrations indicate dipole-dipole cancellation or the formation of multimers between n-Octanol and DMF molecules. Additionally, the effective Kirkwood correlation factor shows a shift towards antiparallel dipole orientations with increasing n-Octanol concentration, indicating the formation of H-bonded heterostructures in the binary mixture, which reduces the effective dipole moment compared to pure liquids. These findings provide valuable insights into the concentration-dependent dielectric properties and molecular interactions in n-Octanol and DMF mixtures. ***Chapter 6*** investigates the ultrasonic velocity, density, and viscosity of n-Hexanol and N, N-Dimethylformamide (DMF) mixtures across the entire composition range ($0.0 \rightarrow 1.0$) at temperatures of 293.15 K, 303.15 K, and 313.15 K. The experimental results showed good agreement with literature values for ultrasonic velocity and viscosity at the studied temperatures. Nonlinear variations in these measured properties at all temperatures suggest the presence of specific intermolecular interactions between the components of the mixture. The trends observed in acoustic and thermodynamic parameters with varying concentrations of n-Hexanol provide insights into the nature of the intermolecular forces present. Various physico-chemical parameters, including adiabatic compressibility, intermolecular free length, acoustic impedance, molar sound velocity, molar compressibility, relaxation time, surface tension, and thermal conductivity, were calculated. These parameters indicate strong intermolecular interactions, primarily due to dipole-dipole and dipole-induced dipole interactions, facilitated by hydrogen bonding. Positive and negative changes in the excess values of acoustic parameters with concentration and temperature confirm interactions between dissimilar molecules. Infrared spectral analysis further emphasized the dominant role of DMF in promoting molecular association, with shifts in the position and intensity of IR bands indicating molecular interactions in the liquid mixtures. ***Chapter 7*** explores the concentration-dependent behaviors of ultrasonic velocity (Uv), density (ρ), and viscosity (η) in the n-Octanol and N, N-Dimethylformamide (DMF) binary system at temperatures of 293.15 K, 303.15 K, and 313.15 K. The experimental results show good agreement with literature values for these properties. Non-linear variations in parameters such as adiabatic compressibility (β), intermolecular free length (L_f), surface tension (σ), and relaxation time (τ) provide insights into the molecular interactions and complex formation via hydrogen bonding between solute molecules. The contrasting shifts in excess acoustic parameters with concentration and temperature further support the presence of interactions between dissimilar molecules. Thermodynamic analysis reveals Arrhenius-type behavior, with positive activation Gibbs energy (ΔG) indicating specific intermolecular interactions, particularly hydrogen bonding and dipolar interactions. The negative activation entropy (ΔS) suggests increased molecular ordering during viscous flow, while the activation enthalpy (ΔH) shows a decrease in the n-Octanol-rich region and an increase in the DMF-rich region, indicating differing energy requirements for the formation of activated species in these regions. ***Chapter 8*** investigates the density (ρ) and refractive index (n) of the n-Hexanol + DMF binary mixture across the entire composition range (0.0 → 1.0) at temperatures of 293.15 K, 303.15 K, and 313.15 K. The experimental results show good agreement with literature values for both properties. The study finds that atomic polarization decreases as the mole fraction of n-Hexanol decreases, with molar volume, polarizability, and molecular radii increasing with the volume fraction of n-Hexanol. The excess refractive index $(n)^E$ shows a negative deviation at all temperatures, with the lowest value around 0.38 mole fraction of n-Hexanol at 303.15 K, indicating weak molecular interactions, likely due to hydrogen bond disruption when DMF is mixed with n-Hexanol. The negative deviation in excess refractive index and excess molar volume decreases with increasing temperature, suggesting weaker interactions. The positive excess reduced molar free volume indicates weak intermolecular interactions with less efficient molecular packing. The negative deviation in internal pressure suggests that repulsive forces dominate over attractive forces. Infrared (IR) spectral analysis supports these findings, revealing molecular associations in the mixtures. The Lorentz-Lorentz (L-L) relation best predicts the refractive index, while the ultrasonic velocity predictions are most accurate at lower temperatures using Nomoto's relation and at higher temperatures using the Van Dael and Vangeel Ideal Mixing Relation. The Arrhenius-Eyring relation provides the most accurate viscosity predictions for both n-Hexanol + DMF and n-Octanol + DMF systems, while other models show higher deviations.

9.2 Future Scopes

Future research could further extend this study by exploring the dielectric, ultrasonic, volumetric, and refractometric properties of binary mixtures involving DMF and long-chain alcohols such as n-Nonanol, n-Decanol. These systems would provide valuable insights into how alkyl chain length and molecular branching influence dielectric relaxation, viscosity, and ultrasonic velocity, shedding light on the role of molecular size, shape, and intermolecular interactions. Advanced spectroscopic techniques, such as Raman and FTIR spectroscopy, could be used to investigate hydrogen bonding, molecular conformation, and solvation dynamics at the molecular level, while NMR spectroscopy (1H-NMR and 13C-NMR) would offer further understanding of local molecular environments and mobility. Molecular dynamics simulations would complement experimental data, allowing for a deeper exploration of hydrogen bonding, solvation structures, and diffusion coefficients, particularly at varying temperatures and concentrations. High-frequency dielectric spectroscopy, extending into the microwave and terahertz ranges, could provide insights into fast molecular dynamics and short-range interactions, while a comprehensive thermodynamic analysis using calorimetric techniques like DSC would quantify the enthalpy and entropy contributions to molecular interactions. This multifaceted approach would facilitate a more thorough understanding of the physicochemical properties of these mixtures, optimizing their applications in chemical, pharmaceutical, and material science industries.