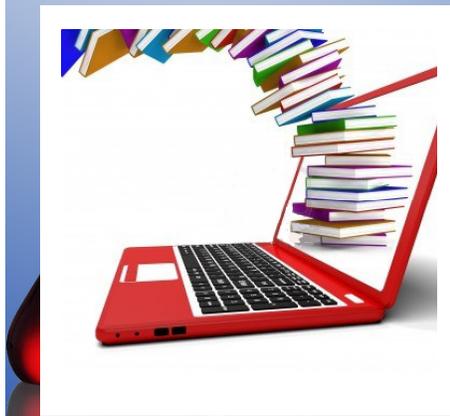


Chapter 2

BRIEF SURVEY OF LITERATURE



CHAPTER-2

BRIEF SURVEY OF LITERATURE

In this chapter literature survey related to the present work on viscosity and ultrasonic velocity have been incorporated

2.1: VISCOSITY STUDIES

Sankara Reddy, et al.¹ have measured the excess volumes, speeds of sound and viscosities at 303.15 K for the binary mixtures of di isopropyl ether (DIPE)+ methyl acetate (MA)+ ethyl acetate (EA) butyl acetate (BA) and+ iso amyl acetate (IAA) as a function of mole fraction over the entire range of composition. Speeds of sounds were evaluated using Jacobson free length theory and Schaaffs collision factor theory.

The data on excess volume (V^E), density (ρ), viscosity (η) and speeds of sound (u) for the binary mixtures of tert-butylamine (TBA) + methyl acetate (MA), + ethyl acetate (EA), + butyl acetate (BA) and + isoamyl acetate (IAA) at 303.15 K experimentally over the entire range of composition have measured by Sankara Reddy, et al.². Speeds of sound were evaluated using Jacobson's free length theory (FLT) and Schaaffs' collision factor theory (CFT). The viscosity data were analyzed on the basis of the corresponding states approach and the Grunberg and Nissan treatment.

Haro, et al.³ have measured the densities and speeds of sound for the ternary system 1-butanol+ 1, 4-dioxane + cyclohexane at the temperatures of 298.15 and 313.15 K. Excess molar volumes and excess isentropic compressibilities have been calculated from experimental data and fitted to the Redlich-Kister equation for ternary mixtures.

Harsha Kumar, et al.⁴ have measured densities and speeds of sound for the binary liquid mixture of cyclopentane with 2-propanol, 1-butanol and 2-butanol over the whole composition range at different temperatures and atmospheric pressure using Anton Paar DSA 5000 densimeter. The experimental results are discussed in terms of molecular interactions present between the unlike molecules.

Gowrisankar, et al.⁵ have measured the density, ultrasonic velocity of sound and viscosity of binary mixtures of N, N- dimethyl aniline (N,NDMA) with 1-propanol, +2- propanol, +1-butanol, +2-butanol, +1-pentanol, +2-methyl-1-propanol, +2-methyl-2-propanol at 303.15 K. The excess/deviations were fitted to Redlich-

Kister equation and the results were analyzed in terms of specific interactions present in these mixtures.

Sreehari Sastry, et al.⁶ have measured the density (ρ), viscosity (η), and speed of sound (U) values for the binary liquid mixture systems of methyl benzoate + 2-propanol and ethyl benzoate + 2-propanol including those of pure liquids over the entire mole fraction range at different temperatures (303.15, 308.15, 313.15, 318.15, and 323.15) K. From these experimentally determined values, various thermo-acoustic parameters have been calculated. The deviations for excess thermo-acoustic parameters have been explained on the basis of the intermolecular interactions present in these binary mixtures.

Siva Prasad, et al.⁷ have determined the Ultrasonic speeds and isentropic compressibilities of aqueous solutions of water + 2-butoxyethanol (2BE) + t-butanol at 298.15 K. The concentrations of t-butanol at which the ultrasonic speed becomes maximum and isentropic compressibility becomes minimum are found to decrease with increases in the concentration of 2BE, X_{2BE} , in the co solvent (aqueous 2BE).

Praveen, et. al.⁸ have measured the Ultrasonic velocity, density, refractive index and viscosity of binary mixtures of aniline with acetic acid (AA) and propionic acid (PA) have been measured at different temperatures over the entire composition range.

Mahendra nath Roy, et al.⁹ have measured the densities and viscosities for binary mixtures of iso amyl alcohol with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol over the entire range of composition at 303.15 K, 313.15 K, and 323.15K and ultrasonic speeds and refractive indices at 303.15 K under atmospheric pressure. From the experimental values of density, viscosity, ultrasonic speed, and refractive index, the values of excess molar volume (V^E), viscosity deviations ($\Delta\eta$), deviations in isentropic compressibility (ΔK_S), and excess molar refraction (ΔR_m) have been calculated. The excess or deviation properties were found to be either negative or positive, depending on the molecular interactions and the nature of liquid mixtures.

Jareena, et al.¹⁰ have measured the density (ρ), speed of sound (u) and viscosity (η) for the binary mixtures of N-ethyl aniline with 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol over the entire composition range at 303.15, 308.15, and 313.15 K. The results have been analyzed in terms of solute – solvent interactions.

The experimental viscosity data of all the binary mixtures were used to test the semi-empirical relations of Grunberg-Nissan, Katti-Chaudhri, and Hind.

Harsha Kumar, et al.¹¹ have measured the densities and speeds of sound for binary mixtures of diethylene glycol monomethyl ether and triethylene glycol monomethyl ether with 3-methyl-1-butanol and 2-methyl-2-butanol at 288.15, 298.15 and 308.15 K, over the entire range of compositions at atmospheric pressure, using an Anton Paar DSA 5000 density meter. The experimental densities and speeds of sound have been used to calculate excess molar volumes and excess molar isentropic compressibilities. The speed of sound data are compared with theoretical speeds of sound calculated using several approaches

Kinart, et al.¹² have measured the densities (ρ) and relative permittivities (ϵ) of numerous binary mixtures of 2-methoxyethanol (ME) (1) + diethyl amine (DEA) (2) at four temperatures and 2-methoxyethanol (1) + triethylamine (TEA) (2) at five temperatures, between (291.15 and 313.15) K, These experimental results are used to disclose the nature of binary interactions in the bulk of studied the binary mixtures.

Kinart, et al.¹³ have measured the relative permittivities (ϵ) and densities (ρ) of numerous binary mixtures of dipropylene glycol monomethyl ether (1) + propylene glycol mono n-butyl ether (2) and dipropylene glycol monomethyl ether (1) + dipropylene glycol mono n-butyl ether (2) at five temperatures, between (293.15 and 313.15) K, The excess molar volumes (V^E) and the relative permittivity deviations ($\Delta\epsilon$) were calculated from these experimental data. The results are discussed in terms of intermolecular interactions in the bulk of studied the binary mixtures.

Chandra Sekhar, et al.¹⁴ have measured the densities (ρ), refractive indices (n_D) and speeds of sound (u) for the binary mixtures of 2-chloroaniline with butanols (1-butanol, 2-butanol) over the entire range of mole fraction at 303.15, 308.15, 313.15 and 318.15 K under atmospheric pressure.

Anjali Awasthi and Ashees Awasthi¹⁵ have measured the viscosity (η) of formamide (FA) with 2-methoxyethanol (2-ME) and 2-ethoxyethanol (2-EE) at 303.15, 308.15, 313.15, 318.15 and 323.15 K over the entire composition range. From the experimental viscosity data, viscosity deviations ($\Delta\eta$) of binary mixtures were evaluated and fitted to the Redlich–Kister equation. The $\Delta\eta$ values are positive over the entire range of composition for (formamide + 2-methoxyethanol) and (formamide + 2-ethoxyethanol) systems. The Grunberg–Nissan (d_{12}), Tamura–Kurata (T_{12}) and

Hind (H_{12}) interaction parameters have been calculated. Furthermore, Gibbs free energy of activation (ΔG^{*E}), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and excess Gibbs free energy of activation (ΔG^{*E}) of viscous flow have also been evaluated by using Eyring viscosity equation. The results are discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules. It is observed that the strength of intermolecular interaction between FA and 2-alkoxyethanol molecules is in order: FA + 2-EE > FA + 2-ME.

Jeevanatham et al.¹⁶ have measured the densities (ρ), viscosities (η) and refractive indices (n_D) for the binary mixtures of o- and m-chloroaniline with 2-alkoxyethanols like 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol at 303.15 K. From the experimental data, the values of excess molar volume (V^E), deviation of viscosity (η^E), deviation of refractive index (Δn^D), excess molar refraction (R_m^E) and excess Gibbs free energy (ΔG^{*E}) for the six binary mixtures were calculated and the values are fitted to Redlich–Kister polynomial equation. The values of all calculated parameters of the binary mixtures and their deviations indicate a strong specific type of interaction between the amino group (single bond NH_2) of chloroanilines with hydroxyl group (single bond OH) of 2-alkoxyethanols.

Mahendra Nath Roy. et al.¹⁷ have measured the densities and viscosities for the binary mixtures of cyclohexylamine and cyclohexanone with butyl acetate, butanone, butyl amine, tert-butylamine, and 2-butoxyethanol at 298.15 K over the entire composition range. From density data, the values of the excess molar volume (V^E) have been calculated. The experimental viscosity data were correlated by means of the equation of Grunberg–Nissan. The density and viscosity data have been analyzed in terms of some semi empirical viscosity models. The results are discussed in terms of molecular interactions and structural effects. The excess molar volume is found to be either negative or positive depending on the molecular interactions and the nature of the liquid mixtures and is discussed in terms of molecular interactions and structural changes.

Amaledu Pal, et al.¹⁸ have measured the speeds of sound (u) have been measured at 298.15 K and atmospheric pressure, as a function of composition for seven binary liquid mixtures of propylamine ($CH_3CH_2CH_2NH_2$, PA) + ethylene glycol monomethyl ether (2-methoxyethanol, $CH_3(OC_2H_4)OH$, EGMME); + diethylene glycol monomethyl ether [{"2-(2-methoxyethoxy)ethanol}],

CH₃(OC₂H₄)₂OH, Di-EGMME]; + triethylene glycol monomethyl ether [{2-(2-(2-methoxyethoxy) ethoxy) ethanol}, CH₃(OC₂H₄)₃OH, Tri-EGMME]; + diethylene glycol mono ethyl ether [{2-(2-ethoxyethoxy) ethanol}, C₂H₅(OC₂H₄)₂OH, Di-EGMEE]; + diethylene glycol monobutyl ether [{2-(2-butoxyethoxy) ethanol}, C₄H₉(OC₂H₄)₂OH, Di-EGMBE]; + diethylene glycol diethyl ether [bis(2-ethoxyethyl) ether, C₂H₅(OC₂H₄)₂OC₂H₅, DEGDEE]; and + diethylene glycol dibutyl ether [bis(2-butoxyethyl) ether, C₄H₉(OC₂H₄)₂OC₄H₉; DEGDBE] using a Nusonic velocimeter based on the sing-around technique. These values have been combined with densities derived from excess molar volumes to obtain estimates of the molar isentropic compressibility K_S , and their excess values K_S^E . The K_S^E , m values are shown to be negative for all mixtures over the entire composition range. The deviations u^D of the speeds of sound from the values calculated for ideal mixtures have been obtained for all estimated values of mole fraction x_1 . The change of K_S^E , m and u^D with composition and the number of –OC₂H₄ – units in the alkoxyethanol are discussed with a view to understand some of the molecular interactions present in alkoxyethanol – propylamine mixtures. Also, theoretical values of the molar isentropic compressibility of K_S , and of the speed of sound u^D have been calculated using the Prigogine-Flory-Patterson (PFP) theory with the van der Waals potential energy model, and the results have been compared with experimental values.

Amalendu Pal and Rekha Gabba¹⁹ have measured the densities, ρ , and speeds of sound, u , have been measured as a function of composition for binary liquid mixtures of dipropylene glycol monopropyl ether (DPGMPE) with n-butyl amine (BA), dibutylamine (DBA), and tributylamine (TBA) at (288.15, 293.15, 298.15, 303.15, and 308.15) K and atmospheric pressure using an Anton Paar DSA-5000 instrument. The ρ and u values were used to calculate excess molar volumes, V^E , deviations from the ideal behavior of the thermal expansion coefficient, α^E , and the isentropic compressibilities, ΔK_S . Moreover, the apparent molar volume, and apparent molar compressibility of the components have been calculated at infinite dilution. The Jouyban–Acree model is used to correlate the experimental values of density and ultrasonic speed at different temperatures.

Ayasen, et al.²⁰ have measured the densities of binary mixtures of 2-methoxyethanol (2-MeO-EtOH) and 2-ethoxyethanol (2-EtO-EtOH) with hexylamine (HLA), diethyl amine (DEA), triethylamine (TEA), tert-butylamine (TBA), aniline (ANL), and benzyl amine (BLA) at varying compositions of the alkoxyalkanols at

298.15 K. The excess molar volumes, V^E , of the binary mixtures were calculated from the experimental density data of the mixtures and the component single solvents. The calculated excess molar volumes were fitted into the Redlich-Kister polynomial to obtain the fitting coefficients and standard deviations. The excess molar volumes of the binary mixtures of all the solvent systems investigated were negative over the entire range of the solvents composition. The negative values were attributed to stronger hydrogen bond formations between the unlike molecules of mixtures than those between the like molecules of the pure components. The magnitude of the excess molar volumes of the binary mixtures of 2-methoxyethanol and the aliphatic amines were in the order TBA > TEA > DEA > HEA. For the two aromatic amines, the magnitudes were in the order BLA > ANL. For binary mixtures of the amines and 2-ethoxyethanol, the magnitudes were in the order DEA > TEA > TBA > HEA at compositions where the mole fraction of 2-EtO-EtOH was ≤ 0.5 and TBA > TEA > DEA > HEA above 0.5 mole fraction of 2-EtO-EtOH.

Pal and Rekha²¹ have measured the densities, ρ , and speeds of sound, u , as a function of composition for binary liquid mixtures of dipropylene glycol monopropyl ether (DPGMPE) with n-butyl amine (BA), dibutylamine (DBA), and tributylamine (TBA) at different temperatures. The results indicated the effect of primary, secondary and tertiary reactivity's of butyl amine with ether and intermolecular interaction between unlike molecules increase in the following order.

Tri butyl amine + Ether > Di butyl amine + Ether > n- butyl amine + Ether

A. K. Nain²² have measured the densities and volumetric properties of binary mixtures of formamide with 1-butanol, 2-butanol, 1, 3- butanediol and 1, 4-butanediol at temperatures between 293.15 and 318.15 K. It was calculated from the excess properties of these mixtures that intermolecular interactions are existing between unlike molecules of the binary liquid mixtures.

Pal and Kumar²³ have measured the excess molar volumes and viscosities for binary mixtures of alkoxypropanols with 1-alkanols at 298.15 K. The V^E are negative for the mixtures investigated. Sign and magnitude of V_m^E and viscosity deviations were used to analyses the mixture behavior of the components.

AlTuwaim, et al.²⁴ have measured the physico-chemical properties of binary mixtures of N, N-dimethylformamide with 1-octanol, 1-nonanol and 1- decanol at different temperatures. The results indicated that as the chain length of alcohol

increased the intensities of the molecular interactions increased between the unlike molecules in the binary liquid mixture under study.

Venkatramana, et al.²⁵ have measured the thermodynamic properties of binary mixtures containing 1-alkanols and discuss the presence of molecular interactions between different liquid mixtures.

Pal and Kumar²⁶ have measured the excess molar volumes and viscosities of binary liquid mixtures of n-alkoxyethanol + 1-propanol systems at 298.15, 308.15 and 318.15 K. The results revealed the presence of intermolecular interaction between the components.

Sinha²⁷ has measured the excess molar volumes, viscosity deviations and speeds of sound for some alkoxyethanols and amines in cyclohexanone at 298.15 K. The excess properties like V_m^E , $\Delta\eta$ and ΔK_s were calculated. The excess properties were fitted to Redlich-Kister polynomial equation. The various properties were discussed in terms of molecular and structural changes.

Sarkar and Roy²⁸ have measured the Investigation on viscous synergism and antagonism prevailing in binary mixtures of cyclohexylamine with isomeric butanols by volumetric, viscometric, refractive index and ultrasonic speed measurements.

González²⁹ has measured the thermodynamics of mixtures containing amines and morpholine liquid mixtures to study the presence of intermolecular between the components.

Roy, et al.³⁰ have measured the solution properties of binary mixtures of some industrially important solvents with cyclohexylamine and cyclohexanone at 298.15 K,” to study the solute – solvent interactions in these liquid mixtures.

Pal, et al.³¹ have measured the densities, excess molar volumes, speeds of sound, and isothermal compressibilities for 2-(2-hexyloxyethoxy) ethanol + n-alkyl amine at temperatures between 288.15 K and 308.15 K. The change of V_m^E and K_s^E with composition and temperature are discussed with a view to understand the molecular interactions present in alkoxyethanol and alkyl amine mixtures.

Oswal and Desai³² have measured the viscosity and excess molar volume of binary mixtures: 4. 1-Alkanol + tri- butyl amine mixtures at 303.15 and 313.15 K. to study the intermolecular interactions present in these binary liquid mixtures.

Oswal³³ has measured the viscosity and excess molar volume of binary mixtures: 5. Characterization of excess molar volume of 1-alkanol with alkyl amines,

dialkylamines and trialkylamines in terms of the ERAS model. The results obtained reveal a strong cross association between the unlike molecules in the mixture resulting from strong negative values for the hydrogen bonding energy and the hydrogen bonding volume.

Oswala and Ijardar³⁴ have measured the partial molar volumes of alkyl amine in non-electrolyte solvents III: alkyl amines in butanols at 303.15 K. The results are interpreted in terms of solute solvent interactions and structural effects of the molecules. The results agree with the different approaches used.

Dubey and Kumar³⁵ have measured the thermo physical properties of binary liquid mixtures of amine and alcohols at various temperatures. The variation of the excess parameters with composition was discussed from view point of intermolecular interactions in these mixtures. The excess properties were either positive or negative depending on interactions.

Dubey and Kumar³⁶ have measured thermodynamic, thermo physical and partial molar properties of liquid mixtures of diethylenetriamine with alcohols at 293.15 to 313.15K. The excess properties were calculated from density and speed of sound. The excess properties were fitted to Redlich- Kister type equation. The viscosity data were correlated to equation of Gurnberg-Nissan.

Ahmad, et al.³⁷ have measured the three excess properties of binary liquid mixtures of 1-butylamine with some alcohols at two different temperatures and studied the interactions present in the liquid mixtures.

Saxena, et al.³⁸ have measured the densities, viscosities and ultrasonic studies of binary liquid mixture of ethylamine and benzyl alcohol at different temperatures and discussed the presence of intermolecular interactions between component liquids.

Kwaterski, et al.³⁹ have measured the excess molar volumes and excess molar enthalpies of binary and ternary mixtures of 1-butanol, a tertiary amine (tri-n-butyl amine or tri-n-octylamine) and n-hexane: experimental results and ERAS-model calculations.

Kinart, et al.⁴⁰ have measured the densities and relative permittivities for mixtures of 2- methoxyethanol with DEA and TEA, at various temperatures and reported the effect of chain length of amines in the determination of molecular interactions.

Pandey and Awasthi,⁴¹ have measured the Acoustic, volumetric and spectroscopic investigations in binary mixtures of formamide/N-methylformamide +

2-chloroethanol at various temperatures. From the experimental values of Ultrasonic velocity and density, the various acoustical parameters have been evaluated. The excess properties were also calculated.

Sankara Reddy, et al.⁴² have measured excess volumes, speeds of sound and viscosities for binary mixtures of n-butyl amine (NBA) with methyl acetate (MA), ethyl acetate (EA), butyl acetate (BA) and isoamyl acetate (IAA) at 303.15 K over the entire range of composition. The experimental results on excess volume, deviation in isentropic compressibility and in viscosity were discussed in terms of molecular interactions between unlike molecules. A Redlich–Kister type equation was used to fit the experimental data on excess volume, deviations in compressibility and viscosity.

Sheng Fang, et al.⁴³ have measured the densities (ρ) and viscosities (η) for binary mixtures of tri-n-octylamine (TOA) + n-heptane, TOA + n-octane, TOA + n-nonane, and TOA + n-decane at different temperatures and at atmospheric pressure. The excess molar volume is calculated from the density data and is correlated by a Redlich–Kister type equation. The excess molar volume is negative for all the four systems. The results show that the volume accommodation effect is predominant in these systems.

Xin-Xue Li, et al.⁴⁴ have measured the densities and viscosities have as a function of composition for the binary liquid mixture of diethylene glycol monomethyl ether $\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$ + water at $T = (293.15, 303.15, 313.15, 323.15, 333.15)$ K under atmospheric pressure. The results suggest that molecular interaction between diethylene glycol monomethyl ether and water is strong. The data have been correlated by the Redlich–Kister type equation.

Oswal and Desai⁴⁵ have investigated the excess molar volume V^E , viscosity deviation $\Delta\eta$, excess viscosity η^E , and excess Gibbs energy of activation G^{*E} of viscous flow from the density ρ and viscosity η measurements of eight binary mixtures of butyl amine with ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol and decanol over the entire range of mole fractions at 303.15 and 313.15 K.

The systems studied exhibit very strong cross association through strong $\text{O-H}\cdots\text{N}$ bonding between $-\text{OH}$ and $-\text{NH}_2$ groups. As a consequence of this strong Intermolecular association, all eight systems have very large negative volumes V^E .

except butyl amine + ethanol mixture, the magnitude of negative deviations in viscosity increases with chain length of alkanol.

Kinarta, et al.⁴⁶ have determined the densities of binary mixtures containing 2-methoxyethanol with n-butyl amine, sec-butyl amine and tert-butylamine at different temperatures, over the complete concentration range. Excess molar volumes were calculated and the departure from ideal behaviour is explained on the basis of specific interactions between the components in these mixtures. Amalendu Pal, et al.⁴⁷ have measured the excess molar volumes (V^E) and dynamic viscosities (η) of binary liquid mixtures of 2-(2-butoxyethoxy) ethanol with dichloromethane, trichloromethane, and tetra chloromethane as a function of composition at 298.15 K and atmospheric pressure. All the mixtures show positive values of $\ln \Delta\eta$ and G^{*E} over the entire concentration range. The results for V^E , $\ln \Delta\eta$, and G^{*E} are discussed on the basis of molecular interactions between the components of the mixtures.

Krishnaiah et al.⁴⁸ has measured the excess volume data for the binary liquid mixtures of butyl amine with aromatic and aliphatic hydrocarbons as a function of composition dilatometrically at 303.15 K and 313.15 K and the results are discussed from the view of intermolecular interactions present between the molecules.

Pius K. et al.⁴⁹ have determined the density and shear viscosity of mixtures of tert-butyl alcohol (BuOH) and tert-butylamine (TBA) with water for various temperatures at (288 to 318 K for H₂O + BuOH and 288 to 308 K for H₂O + TBA) over the whole composition range. Excess molar volumes and apparent molar volumes of the components of each system were calculated from the density data. In both systems the apparent molar volume of the organic component passes through a minimum in the water-rich region. Both systems exhibit large negative excess molar volumes which are essentially independent of temperature at all composition.

Mahindra Nath Roy et al.⁵⁰ have measured the densities and viscosities were measured for the binary mixtures of cyclohexylamine and cyclohexanone with butyl acetate, butanone, butyl amine, tert-butylamine, and 2-butoxyethanol at 298.15K over the entire composition range. From density data, the values of the excess molar volume (V^E) have been calculated. The results are discussed in terms of molecular interactions and structural effects. The excess molar volume is found to be either negative or positive depending on the molecular interactions and the nature of the

liquid mixtures and is discussed in terms of molecular interactions and structural changes.

Ismael, et al.⁵¹ has measured the densities and speeds of sound for the systems 2-, ethoxy ethanol (2ME) + ethoxyethanol (2EE), or + 2-butoxyethanol (2BE), or + 2-(2-methoxyethoxy) ethanol (2MEE) and for the 2-propoxyethanol (2PE) + dibutylether (DBE) mixture at 293.15, 298.15, and 303.15 K and atmospheric pressure using a vibrating-tube densimeter and results are analyzed using the intermolecular interactions present between the unlike molecules.

Naved I. Malek, et al.⁵² have measured the densities ρ and speeds of sound for pure 1-hexyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_6\text{mim}][\text{BF}_4]$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_8\text{mim}][\text{BF}_4]$), butyl amine (BA), and octylamine (OA) from (293.15 to 323.15) K and binary mixtures of the ionic liquids (ILs) with amines at (298.15, 308.15, and 318.15) K. The isentropic compressibilities, κ_S , Rao's molar sound functions, R , intermolecular free lengths, L_f , excess molar volumes, V_m^E , and excess isentropic compressibilities, K_S^E for binary mixtures were derived. The V_m^E and K_S^E of the binary mixtures are negative and decrease with increasing temperature, with the exception of V_m^E being positive for $[\text{C}_6\text{mim}][\text{BF}_4]$ and $[\text{C}_8\text{mim}][\text{BF}_4]$ + OA in the high IL mole fraction region. The Prigogine–Flory–Patterson (PFP) theory has been applied to interpret the u and V_m^E data.

Wen -Lu weng, et al.⁵³ have measured the viscosities and densities for the binary mixtures of benzyl amine with 1-pentanol, 2-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol at temperatures from 298.15 K to 308.15 K. Redlich–Kister type equations were fitted to the isothermal excess molar volumes and viscosity deviations, and the kinematic viscosity data were correlated with the McAllister equation.

Wen-Lu weng and Jui-Tang Chen,⁵⁴ have measured the densities and viscosities for the binary mixtures of n-butyl amine with 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 2-methyl-2-pentanol, and 4-methyl-2-pentanol at 303.15 K, 313.15 K, and 323.15 K over the entire composition range. Excess volumes and viscosity deviations were calculated at various temperatures. Both excess molar volumes and viscosity deviations are negative for all investigated systems. A Redlich–Kister-type equation was fit to the isothermal excess molar volumes and viscosity deviations, and McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities.

Rama Murthy Palepu, et al.⁵⁵ have determined the densities and viscosities for the binary systems of m-cresol with aniline, N-methyl aniline, N,N-dimethylaniline, N-ethyl aniline, and N,N-diethyl aniline at five different temperatures. From the experimental results, the excess volume, excess viscosity, excess molar free energy of activation of flow, excess partial molar volume, and partial molar volumes were calculated. Also various thermodynamic η parameters of activation of flow were calculated from the dependence of viscosity on temperature. The deviations from ideality of thermodynamic and transport functions are explained on the basis of molecular interactions between the components of the mixture.

Amalendu Pal and Rakesh kumar Bhardwaj⁵⁶ have measured the excess molar volumes (V^E) and dynamic viscosities (η) as a function of composition for binary liquid mixtures of propylamine with 2,5-dioxahexane, 2,5,8-trioxanonane, 2,5,8,11-tetraoxadodecane, 3,6,9-trioxaundecane, and 5,8,11-trioxapentadecane at 298.15 K and the presence of intermolecular interactions between unlike molecules have been discussed through η^E , V^E and G^E values.

Amalendu pal and Sanjay Sharma⁵⁷ have measured the excess molar volumes (V^E) and dynamic viscosities (η) for five (alkoxyethanol + propylamine) mixtures as a function of composition at 298.15 K and atmospheric pressure. The alkoxyethanols were 2-methoxyethanol, 2-(2-methoxyethoxy) ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy) ethanol, and 2-{2-(2-methoxyethoxy) ethoxy} ethanol. The excess molar volumes (V^E) are all negative over the whole composition range. The viscosity data have correlated by the methods of Kendall and Monroe, Grunberg and Nissan, Tamura and Kurata, Hind, Katti and Chaudry, and with McAllister correlations. From the experimental data, deviations in the viscosity ($\Delta\eta$) have calculated. The results are discussed in terms of the interaction between components.

Juan Antonio Gonzalez, et al.⁵⁸ Alkoxyethanol + alkane systems examined in the framework of the ERAS model. An exact expression for the molar excess heat capacity at constant pressure, C_p^E , of solutions formed by a self-associated compound and an inert solvent has derived. The C_p^E and the molar excess enthalpies (H^E) and excess volumes (V^E), as well as the molar enthalpies of vaporization of the pure alkoxyethanols, are represented accurately by ERAS. The calculated curves for H^E and V^E are skewed towards high mole fractions of the alkanes. The experimental curves are more symmetrical. The opposite behaviour is observed for C_p^E in solutions with 2-ethoxyethanol, 2-propoxyethanol, or 2-butoxyethanol. The

differences between the experimental and theoretical values arise because ERAS does not properly take into account the enhanced dipole–dipole interactions due to the formation of intermolecular H-bonds in alkoxyethanols.

Letcher⁵⁹ have measured the excess volumes of a primary amine (*n*-propylamine and *n*-butyl amine), or a secondary amine (diethyl amine, di-*n*-propylamine and di-*n*-butyl amine), or a tertiary amine (triethylamine, tri-*n*-propylamine, and tri-*n*-butyl amine) + chlorocyclohexane, + nitrocyclohexane, and + methylcyclohexane over the whole composition range at 298.15 K.

Oswal and Ijardar⁶⁰ have measured the viscosities η of dilute solutions of *n*-propylamine, *n*-butyl amine, di-*n*-propylamine, di-*n*-butyl amine, triethylamine, tri-*n*-propylamine, and tri-*n*-butyl amine in 1-butanol and 2-butanol at 303.15 K. The strong solute–solvent interactions leading to the structure formation between butanol and alkyl amine molecules through H-bondings are observed from the results. .

Isamael Mozo , et al.⁶¹ have measured the densities, ρ , and speeds of sound, u , of systems formed by 2-(2-methoxyethoxy)ethanol (22MEE), 2-(2-ethoxyethoxy)ethanol (22EEE) or 2-(2-butoxyethoxy)ethanol (22BEE) and dibutylether (DBE) at 293.15, 298.15 and 303.15 K and atmospheric pressure using a vibrating-tube densimeter .The results indicates that the main contribution to excess function comes from the disruption of the interactions between cellosolve molecules.

Raman⁶² measured the densities and viscosities of 2-methoxyethanol with ethyl acetate and butyl acetate at 303.15 K. The experimental data was used to calculate V^E , Aminabhavi and Gopalakrishna²³ measured densities, viscosities and refractive indices for the binary mixtures of 2-ethoxyethanol with n-alkanes (C₆-C₁₂), 2,2,4-trimethylpentane and cyclohexane over the entire composition range at different temperatures. The computed values of V^E , η^E and molar refractivity are fitted to the Redlich-Kister polynomial equation. The effect of size and shape of the alkanes on excess quantities were discussed.

Oswal and Desai⁶³ have calculated the excess molar volume V^E , the viscosity deviation $\Delta\eta$ and the excess Gibbs energy of activation ΔG^{*E} of viscous flow from density and viscosity measurements of six mixtures of 1-propanol, 1-butanol, 1-pentanol, 1-heptanol, 1-octanol and 1-decanol with tri-*n*-butyl amine over the entire range of mole fractions at 303.15 and 313.15 K. The values of V^E of all six systems are very large and negative. Except for 1-propanol+tri-*n*-butylamine, the magnitude of

negative deviations in viscosity increases with chain length of alkanol. The results have explained considering mixed associated species of type A&B involving alkanol (A) with tri-*n*-butyl amine (B) through OH...N bonds.

Nikam and co-workers⁶⁴ measured densities and viscosities for the binary mixtures of dimethylsulphoxide + methanol, + ethanol, + propan-1-ol, + propan-2-ol, + butan-1-ol, + 2-methylpropan-2-ol at 298.15 and 303.15 K and the results suggest the formation of complexes between the components. The densities, viscosities and refractive indices for binary mixtures of bis (2-methoxyethyl) ether + cyclohexane and for those of bis (2-methoxyethyl) ether + 1, 2, 3, 4-tetrahydrophthalene and 2-ethoxyethanol + propan-1-ol, + propan-2-ol, or + butan-1-ol were measured at various temperatures by Aminabhavi and Gopalakrishna. The experimental results are used to calculate excess molar volume, excess viscosity etc. and these results were fitted to Redlich-Kister polynomial equation to estimate the binary interaction coefficients.

An attempt was made by Pal and Dass⁶⁵ to determine excess molar volumes (V^E) and viscosities (η) as a function of mole fraction for binary liquid mixtures of water + 2-methoxyethanol, + 2-(2-methoxyethoxy) ethanol and + 2-[2-(2-methoxyethoxy)] ethanol at 308.15 K. The results for V^E and η^E were discussed in terms of interactions of water with an amphiphilic molecule.

Pal and Singh⁶⁶ measured the excess molar volumes of $\{x\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH} + (1-x)\text{H}(\text{CH}_2)_V\text{O}(\text{CH}_2)_2\text{OH}\}$ for $V = 1, 2$ and 4 at 298.15 K as a function of composition using a continuous dilution-dilatometer. The results were used to estimate the excess partial molar volumes of the components to find the extent of interactions

A systematic study was carried out by Pal and Singh⁶⁷ to measure the excess molar volumes for binary liquid mixtures containing 2-butoxyethanol and ethylene glycol, diethyleneglycol, triethyleneglycol, propylene glycol and dimethylsulphoxide with the help of the continuous dilution dilatometer over the entire mole fraction range at 313.15 K. The results were used to estimate the extent of deviation from ideal behavior

Aminabhavi and Gopala Krishna, et al.⁶⁸ concluded that the intermolecular interactions are present in the binary liquid mixtures of 2-methoxyethanol with alcohols from their density and viscosity measurements at various temperatures.

Viscosities and densities of binary liquid mixtures containing 2-(2-butoxyethoxy) ethanol with aniline and N-alkyl substituted anilines have been determined by Wiseman, et al.⁶⁹ at five different temperatures. Excess molar volume (V^E), excess viscosity (η^E) and the excess Gibbs free energy of activation of viscous flow (G^E) were calculated and the deviations from ideal behaviour was explained on the basis of specific interactions between the components of the mixture.

Sastry and Raj⁷⁰ reported positive values of excess viscosity and free energy of activation of viscous flow for the binary liquid mixtures of 2-butoxy ethanol with n-Hexane and n-heptane at 303.15 and 313.15 K. Thermodynamic contributions are found to contribute to the observed experimental viscosities. The viscosities of mixture are also found to be reasonably expressed by Gurnberg-Nissan and Ac Allister relations.

Krishnaiah, et al.⁷¹ made a systematic study by measuring excess molar volumes for the mixtures of 2-butoxyethanol with aliphatic alcohols as a function of mole fraction at 308.15 K. From the results they have concluded that the increase in chain length of alcohols, result in an increase in magnitude of excess functions which in turn suggests the strength of molecular interactions between the unlike molecules.

Subha, et al.⁷² calculated excess molar volumes from the measured densities at 303.15 K for the binary liquid mixtures of dimethylsulphoxide with n-butyl amine, sec-butyl amine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine and cyclohexylamine at 303.15 K. The results show the extent of hydrogen bonding between the components.

To report the effect on mixing secondary and primary amines with benzene and substituted benzene, Letcher and Spiteri⁷³ calculated excess molar volumes from the measured densities of the liquid mixtures. They have reported the order of interaction in these mixtures as $C_6H_6 + \text{primary amine} > C_6H_5 + \text{secondary amine}$.

To study in detail the dependence of each thermodynamic property of the binary mixtures of representative aliphatic amines on the other component of binary mixtures, Rao and Suri⁷⁴ measured densities of binary liquid mixtures of triethylamine with benzene, toluene, ethyl benzene and three isomeric xylenes at 313.15 K. From the computed excess volumes the following order of interactions were reported.
m- Xylene > o - Xylene > p - Xylene

2.2: ULTRASONIC VELOCITY STUDIES

A review of literature on acoustical studies of liquid mixtures reveal that ultrasonic velocity measurements are used to understand the nature of intermolecular interactions between the component molecules. The changes in ultrasonic velocity and its derived parameters such as acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free-length (L_f), relative association (R_A), excess parameters for acoustic impedance (Z^E), ultrasonic velocity (u^E), isentropic compressibility (K_s^E) and intermolecular free-length (L_f^E) on the mole fraction of solvent composition are found to be important in studying the intermolecular interactions between the components.

Ultrasonic velocity is an important physical property having structural dependence and provides a unique advantage in evaluating some of the thermodynamic parameters of matter. The field of ultrasonic is so vast, that a review of even the more important works requires an encyclopedic exposition. The author presents here only a brief review of the work done in liquid mixtures pertaining to the studies carried out by him..

Venkatesu, et al.⁷⁵ measured the ultrasonic velocity and density for ternary mixtures of N,N-dimethylformamide, methyl ethyl ketone with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol at 303.15 K and the results were analysed and concluded that induced dipole-dipole interactions are existing due to the polar nature of DMF and alkanols.

Pal and Dass⁷⁶ measured the density and ultrasonic velocity for the binary liquid mixtures of diethylene glycol mono ethyl ether with methanol, ethanol, 1-propanol, 1-pentanol and 1-hexanol at 298.15 K over the entire composition range. From the experimental values, the acoustical parameters u^E and K_s^E were determined. The molecular interactions present between the liquids were discussed from the variations of u^E and K_s^E with composition of liquid mixtures. They have concluded that the interaction decreased with increase in size of the alcohols.

Pal and Sharma⁷⁷ measured the ultrasonic velocities of binary liquid mixtures of 2-methoxyethanol with 2{2-(2-methoxyethoxy) ethoxy} ethanol, 2-{2-(2-ethoxyethoxy) ethoxy} ethanol and 2-{(2-(2-butoxyethoxy) ethoxy} ethanol over the entire composition range at 298.15 K. These results were discussed in terms of the variation of parameters with composition and number of carbon atoms in the aliphatic chain of the alkoxoethanols to explore the molecular interactions in these liquid mixtures.

Aminabhavi and Gopalakrishna⁷⁸ measured the density and velocity in binary mixtures of 2-ethoxyethanol and n-alkanes (C₆-C₁₂), 2, 2, 4-trimethyl pentane and cyclohexane over the entire composition range at different temperatures and results were analysed in view of the effect of the size and shape of the alkanes on excess quantities.

Aminabhavi, et al.⁷⁹ calculated the isentropic compressibility by measuring density and speed of sound of binary liquid mixtures of 2-methoxyethanol with alcohols, at 298.15 K, 303.15 and 308.15 K and the results were used to explain the intermolecular interactions between the component molecules.

Raman⁶² measured the density and speed of sound of 2-methoxyethanol with ethyl acetate and butyl acetate at 303.15 K and the results were analyzed on the basis of Jacobson's free-length theory and Schaaff's collision factor theory.

Prakash and Darbari⁸⁰ measured density and ultrasonic velocity for four binary mixtures of n-octanol and n-decanol with diethyl amine and triethylamine at different compositions at 298.15 K. From the experimental data excess parameters like K_s^E & L_f^E were calculated and the deviations from ideality of these functions were explained on the basis of molecular interactions between the components of the mixture. Excess volume and speed of sound data of binary liquid mixtures of water + 1, 2-ethanediol, + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol are measured at 308.15 K by Krishnaiah, et al.⁸¹ and the results obtained were used to discuss the solute-solvent interactions present in the solutions.

Ali, et al.⁸² have calculated various acoustical parameters from the ultrasonic velocity and density measurements for ethanol + 1-hexanol, ethanol + 1-octanol and acetonitrile + N, N-dimethylformamide at 303.15 K. From the variation of, K_s^E or L_f^E or Z^E parameter with composition of liquid mixture curves, the results were analysed in view of the intermolecular interactions present in the mixtures.

Pal and Singh⁸³ measured speed of sound for the binary liquid mixtures of 2-methoxyethanol with different carbitols over the whole range of mole fraction at 298.15 K and from the measured data excess isentropic compressibility, excess velocity were calculated. The behaviour of u , u^E and K_s^E with composition and number of carbon atoms in the aliphatic chain of alkoxyethanols were discussed. Oswal and Phalak⁸⁴ measured speed of sound in the mixtures of p-dioxane with cyclohexane, n-hexane, benzene, toluene, carbon tetrachloride, chloroform, 1,1,2,2-tetrachloroethane, penta chloromethane and ethyl acetate over the whole mole fraction

range at 303.15 K. The experimental data were combined with the densities and molar volumes to obtain isentropic compressibilities and number. The behaviour of the present mixtures was discussed in terms of possible molecular interactions and Prigogine-Flory-Patterson theory of liquid mixtures.

Rao and Ronald⁸⁵ made systematic study by measuring ultrasonic velocities and densities of binary liquid mixtures of water + 2-butoxyethanol, 2-butoxyethanol + benzene and butoxyethanol + decane at 298.15, 313.15 and 328.15 K. From the measured data apparent molar volume and the adiabatic compressibility parameters were evaluated. The results were discussed in terms of intermolecular interactions between the component molecules.

Experimental studies on ultrasonic velocities of binary liquid mixtures have been carried out by Sharma, et al.⁸⁶ and the results were used to analyse the nature of intermolecular interactions.

2.3: AIM AND SCOPE OF THE PRESENT STUDY

The work presented here deals with the physico-chemical investigations of amines in different carbitols the data is used to understand the intermolecular interactions between unlike molecules.

Literature survey reveals that very few attempts have been made to study the excess properties for mixtures containing amines. So far no attempt has been made to study the excess properties of series of amines with carbitols.

The carbitols chosen are 2-(2-methoxy ethoxy) ethanol, 2-(2-ethoxyethoxy) ethanol and 2-(2-butoxy ethoxy) ethanol, in view of their special industrial importance. 2-(2-methoxyethoxy) ethanol is widely used for various industrial processes⁸⁹ and has unique solvating properties associated with its quasi-aprotic character. 2-(2- ethoxy ethoxy) ethanol, an ether alcohol, is a quite toxic solvent, weak narcotic. 2-(2-butoxyethoxy) ethanol is of particular interest because of its bulk and surface properties that undergo drastic changes with concentration and temperature. It also has a closed miscibility gap when mixed with water.

The presence of etheric group (-O-) and hydroxyl (-OH) group in the same molecule of carbitols accounts for greater miscibility and solvency for a wide range of organic chemicals. The ether group of these compounds promotes solubility of these solvents through hydrogen bonding.

Amines are also very important chemicals used in different industries as solvents, raw materials, intermediates, diluents, fuels and fuel additives etc. The amine chosen constitutes three groups. (1) Normal amines, (2) branched amines and (3) cyclic amines. n-butyl amine, n-hexylamine and n-octylamine which form homologous series of amines come under normal amines. The branched amines include sec-butyl amine and tert-butylamine. Cyclohexylamine comes under cyclic amine group.

The study of binary liquid mixtures of carbitols with above said amines is of particular interest only because of their wide usage as industrial solvents but also from the more fundamental point of view for investigating the effect of the simultaneous presence of etheric and alcoholic groups in the same molecules (i.e. carbitols). No attempts have been made to study the molecular interaction between above said liquid mixtures in terms of thermo physical properties. Hence an attempt has made to investigate the molecular interactions between carbitols and the above said amines on the basis of physical properties such as viscosity, excess viscosity, excess molar volume, excess Gibbs free energy of activation of viscous flow, Gurnburg- Nissan interaction parameter, ultrasonic velocity, isentropic compressibility, acoustic impedance, intermolecular free-length and Relative association and the excess acoustic parameters. Further this study gives information on the effect of dielectric, solubility nature of organic solvents, chain length and the size of the alkoxy group of carbitols. The results are interpreted in terms of self-association and the formation of intermolecular hydrogen bonded complexes.

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