

SUMMARY

The work reported in this thesis deals with the study on the nature and degree of molecular interactions between the components of various binary liquid mixtures through the measurements of excess volume (V^E), isentropic compressibility (κ_s), viscosity (η) and their derived parameters at $T = (303.15 - 318.15)$ K. The systems that are chosen in this investigation contain 3-chloroaniline as common component & di/tri substituted chlorobenzenes, isomeric chlorotoluenes, substituted ethanols and mono substituted benzenes as other components. The di / tri substituted chlorobenzenes chosen in this work are : 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene; isomeric chlorotoluenes are: o-chlorotoluene, m-chlorotoluene and p-chlorotoluene; substituted ethanols are : 2-aminoethanol, 2-chloroethanol and 2-phenylethanol & mono substituted benzenes are: chlorobenzene, bromobenzene and nitrobenzene. The sign and magnitude of the thermodynamic and transport properties have been used to understand the nature and extent of molecular interactions, which are responsible for deviation of actual value from the ideal behaviour.

The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built- in solid-state thermostat and a resident program with an accuracy of temperature of $303.15 \text{ K} \pm 0.02 \text{ K}$. The estimated accuracy in the density measurement was $\pm 2 \times 10^{-5} \text{ gm.cm}^{-3}$. Proper calibration at each temperature was achieved with doubly distilled, de-ionized water and with air as standards. A multi-frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, was used to measure the ultrasonic sound velocities of binary liquid mixtures with an accuracy of $\pm 0.2\%$ at 303.15 K. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled to $303.15 \text{ K} \pm 0.02 \text{ K}$ was used for all the ultrasonic sound velocity measurements. The viscosities of pure liquids and their mixtures were determined at

atmospheric pressure and at temperature 303.15K by using an Ubbelohde viscometer, which was calibrated with benzene and doubly distilled water. The Ubbelohde viscometer bulb had a capacity of 15ml and the capillary tube with a length of about 90 mm with 0.5 mm internal diameter. The viscometer was thoroughly cleaned and perfectly dried and was filled with the sample liquid by fitting the viscometer to about 30° from the vertical and its limbs were closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of ± 0.01 K for about 20 minutes to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty ± 0.01 s was used for flow time measurements. The uncertainty of viscosity thus estimated was found to be ± 0.005 mPa.s

Experimental data on excess volume, excess isentropic compressibility, deviation in viscosity and excess Gibbs energy of activation of viscous flow (G^{*E}) were discussed in terms of the depolymerization, differences in size and shape, loss of dipolar association, hydrogen bonds and charge transfer complex formation. The viscosity data were correlated using equations; Grunberg and Nissan interaction parameter (d_{12}), Katti and Chaudhri interaction parameter (W_{vis}/RT) and Hind interaction parameter (H_{12}), Tamura and Kurata (T_{12}) and Heric and Brewer (Δ_{12}) for the system studied.

Excess volumes, excess isentropic compressibilities and viscosities were measured for 12 binary systems consisting of 3-chloroaniline as common component and di/tri substituted chlorobenzenes (1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene), isomeric chlorotoluenes (o-chlorotoluene, m-chlorotoluene and p-chlorotoluene), substituted ethanols (2-aminoethanol, 2-chloroethanol and 2-phenylethanol), & mono substituted benzenes (chlorobenzene, bromobenzene and nitrobenzene) as other common components.

Excess volumes are negative for the binary systems of 3-chloroaniline with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene and this may be due to

the difference in their shapes which lead to different alignments in the liquid mixtures. Further, the chlorine atom at the 4th position in 1, 2, 4-trichlorobenzene offers, the least steric hindrance to 3-chloroaniline molecules and thus the electron donor – acceptor (charge-transfer complexes) interactions in it are lower than those of 1, 2-dichlorobenzene and 1, 3-dichlorobenzene in the binary liquid mixtures.

The values of V^E for the binary mixtures of 3-chloroaniline with di / tri chlorobenzenes fall in the order:



The above order suggests that the dipole moments of the pure solvents are influencing the V^E data of the binary liquid mixtures. The dipole moments are 3-chloroaniline 2.67D, 1,2-dichlorobenzene: 2.77 D, 1,3-dichlorobenzene: 1.89 D and 1,2,4-trichlorobenzene: 0.8109 D. The more negative V^E data of 1,2-dichlorobenzene when compared with the other chlorobenzenes are due to its high dipole moment that leads to stronger dipole - dipole interactions. This type of behaviour is reported earlier. Hence, the above order may be justified.

The V^E values are negative for the binary systems of 3-chloroaniline with o-chlorotoluene, m-chlorotoluene, and p-chlorotoluene and the negative values may be due to the effects leading to contraction in volume are dominant over the effects leading to expansion in volume for the binary mixtures of 3-chloroaniline with isomeric chlorotoluenes.

The values of V^E for the binary mixtures of 3-chloroaniline with isomeric chlorotoluenes fall in the following order:



The difference in V^E values between o-chlorotoluene, m-chlorotoluene and p-chlorotoluene is probably because of different positions of the chlorine atom in chlorotoluene. As the separation between the two groups' increases, the intermolecular interaction is expected to decrease. The intermolecular interaction in ortho isomer causes a large strain in the ring, resulting an opposite pole at ortho side of the ring and thus giving a more dipolar character, than meta and para derivatives. Thus, the intermolecular interactions in ortho position become stronger than the meta and para isomers due to stronger polar character. Hence, the above order may be justified.

Excess volumes are negative for the binary systems of 3-chloroaniline with 2-chloroethanol, 2-aminoethanol and 2-phenylethanol and they may be attributed to the hydrogen bonding between unlike molecules

The values of V^E for the binary mixtures of 3-chloroaniline with substituted ethanols are in the following order:



The more negative excess volume in the system 3-chloroaniline + 2-aminoethanol reveals that a more efficient packing and/or attractive interactions occurred between these two components when mixed together. Consequently, its structure and smaller size lead to interstitial accommodation with 3-chloroaniline molecules more easily compared to the 3-chloroaniline with 2-chloroethanol, + 2-phenylethanol. Hence the above order is justified.

Excess volumes are negative for binary systems of 3-chloroaniline with bromobenzene, chlorobenzene and nitrobenzene and they may be due to the geometrical fitting of the molecules of different molecular sizes into each other's, electron donor-acceptor type interactions and charge-transfer complexes exist between unlike molecules.

The values of V^E with respect to non-common component fall in the order:

Nitrobenzene < chlorobenzene < bromobenzene

The above order indicates that the electron accepting ability decreases with increasing electron withdrawing halo/group in the substituted benzene derivatives. Hence the said order is justified.

The excess isentropic compressibility (κ_s^E) are negative for the binary systems of 3-chloroaniline with 1,2-dichlorobenzene, +1,3-dichlorobenzene, +1,2,4-trichlorobenzene over the entire composition range at T=(303.15-318.15) K. The negative excess isentropic compressibility (κ_s^E) in the above systems may be due to the decrease in intermolecular free length as a result of mixing, enabling consequently the sound wave to cover longer distance in mixtures compared to pure components.

The values of κ_s^E for the binary mixtures of 3-chloroaniline with di / tri chlorobenzenes fall in the order:

1,2-dichlorobenzene < 1,3-dichlorobenzene < 1,2,4-trichlorobenzene

The above order indicates that the intermolecular interactions in ortho position become more than the meta and para positions and due to which, polar character will be more in ortho position. The effects of increasing temperature results in the decrease of κ_s^E values suggesting the reduction of the specific molecular interactions; κ_s^E data becomes less negative which may be due to low thermal dissociation of hetero-association in liquid mixtures.

The excess isentropic compressibility (κ_s^E) values are negative for binary systems of 3-chloroaniline with o-chlorotoluene, m-chlorotoluene and p-chlorotoluene over the entire composition range at T= (303.15 K - 318.15) K. The negative values may be attributed to the complex formation between the two component molecules which leads to a decrease in intermolecular free length and increase in sound velocities and thereby decreasing the

isentropic compressibilities of the mixtures. This means, that the mixtures are less compressible than the corresponding ideal mixture.

The values of κ_s^E for the binary mixtures of 3-chloroaniline with isomeric chlorotoluenes are found to be in the following order:



The increase in temperature decreases the κ_s^E values and it may be attributed to the reduction in the specific molecular interactions with the rise of temperature. Also, as the temperature increases κ_s^E data become less negative and this may be due to the low thermal dissociation of hetero-association in liquid mixtures.

The excess isentropic compressibility (κ_s^E) values are negative for binary systems of 3-chloroaniline with 2-chloroethanol, 2-aminoethanol and 2-phenylethanol over the entire composition range at T= 303.15- 318.15) K. The observed negative values of κ_s^E indicate the predominance of hydrogen bond interactions between the unlike molecules over the dissociation effects of the mixing components. In the binary mixtures, there is a mutual dissociation of the hydrogen bonded structure present in the pure liquids with subsequent formation of the intermolecular hydrogen bonding between unlike molecules, resulting in a decrease in the compressibility of the mixture, and hence negative κ_s^E values are observed.

The values of κ_s^E for the binary mixtures of 3-chloroaniline with substituted ethanols are in the following order:



The excess isentropic compressibility (κ_s^E) is negative over the entire composition range for the binary mixtures of 3-chloroaniline with mono substituted benzene derivatives at T= (303.15-318.15) K. The observed values of κ_s^E can be qualitatively explained by considering the factors (i) disruption of associated structures / molecular order in the pure

liquids, (ii) the formation of weak bonds by dipole-induced-dipole interaction between unlike molecules, and (iii) free volume changes from mixing of components of different sizes. The first factor contributes positive κ_s^E values, whereas the remaining two factors led to negative κ_s^E values. The resultant negative values of κ_s^E for the binaries indicate the dominance of net combination of factors (ii) and (iii), and that binaries are less compressible than their ideal mixtures.

The values of κ_s^E for the binary mixtures of 3-chloroaniline with mono substituted benzene derivatives are in the following order:

Nitrobenzene < chlorobenzene < bromobenzene

The above order suggests that the extent of interactions between unlike molecules decreases with polarizability value and proper dipole alignment of the components. The negative values of κ_s^E increase with increasing temperature and this suggests that specific interactions increase due to the enhanced thermal energy.

The sign and magnitude of $\Delta\eta$ depend on the combined effect of the factors such as molecular size, shape and intermolecular forces. Fort and Moore observed that the positive viscosity deviation values indicate the specific interactions involving the formation of some kind of hetero-molecular complexes. The viscosity deviation may be generally explained by considering the following factors:

(i) The difference in size and shape of the component molecules and the loss of dipolar association in pure component may contribute to a decrease in viscosity.

(ii) Specific interactions between unlike components such as dipole - dipole interactions and charge transfer complexes may cause for increase in viscosity in mixtures than in pure components.

The former effect produces negative deviation in viscosity and the latter effect produces positive deviation in viscosity.

The viscosity deviation data are positive for the binary systems of 3-chloroaniline with 1,2-dichlorobenzene, + 1,3-dichlorobenzene, + 1,2,4-trichlorobenzene over the entire composition range at $T = (303.15-318.15)$ K. The positive values of viscosity deviation for the binary systems investigated suggest that the hetero-molecular complexes between unlike molecules are relatively more than those of the pure components. The effect of temperature increase is to disrupt hetero and homo association of the molecules resulting in an increase in fluidity of the liquids as is reflected from the higher $\Delta\eta$ values at higher temperatures.

According to Reed and Taylor and Palepu et al. excess Gibbs energy of activation of viscous flow (G^{*E}) may be considered as a reliable criterion to detect or exclude the presence of interaction between unlike molecules. According to these authors, the magnitude of the positive G^{*E} values is an excellent indicators of the strength of specific interactions. The positive values of excess Gibbs energy of activation of viscous flow for the binary systems in the present investigation suggest that the specific interaction between 3-chloroaniline and di /tri substituted chlorobenzene molecules take place through dipole - dipole interactions. Thus, the values of excess viscosity and excess Gibbs energy of activation of viscous flow are dependent on the position of the -Cl group in the di / tri substituted chlorobenzene molecule, indicating a different extent of molecular interactions in di /tri substituted chlorobenzenes.

The viscosity deviation data are positive for the binary systems of 3-chloroaniline with o-chlorotoluene, + m-chlorotoluene, + p-chlorotoluene over the entire composition range at $T = (303.15-318.15)$ K. Fort and Moore attributed the positive deviation in viscosity to the specific interactions involving the formation of hetero-molecular complexes. The deviation in viscosity variation gives a qualitative estimation of the strength of the

intermolecular interactions. The positive values of viscosity deviation for the binary systems investigated suggest that the viscosities of associates formed between unlike molecules are relatively more than those of the pure components.

The excess Gibbs energy of activation of viscous flow values is positive for three binary mixtures of 3-chloroaniline with o-chlorotoluene, + m-chlorotoluene, + p-chlorotoluene over the entire composition range at all investigated temperatures. The positive values of excess Gibbs energy of activation of viscous flow for the binary systems investigated suggest that the specific interaction between 3-chloroaniline and isomeric chlorotoluene molecules take place through dipole - dipole interactions. Thus, the values of deviation in viscosity and excess Gibbs energy of activation of viscous flow are dependent on the position of the -Cl group in the toluene molecule, indicating a different extent of molecular interactions in chlorotoluene molecules.

Deviation in viscosities $\Delta\eta$ are positive for 3-chloroaniline with 2-chloroethanol, 2-aminoethanol and 2-phenyl ethanol over the entire composition range at T = (303.15 to 318.15) K. The positive data for all the binary systems suggests that the viscosity of the mixture is higher than that of the pure components and hence, the fluidity of the mixture is low. This indicates the presence of a specific interaction such as the formation of hetero-associate complexes between unlike molecules. The positive values of deviation in viscosity increase with the increase in temperature in all these systems.

The excess Gibbs energy of activation of viscous flow values is positive for three binary mixtures over the entire composition range at all investigated temperatures. The positive values of excess Gibbs energy of activation of viscous flow for the binary systems investigated suggest the intermolecular association through H-bonding between substituted ethanols and 3-chloroaniline molecules. The positive values of excess Gibbs energy of activation of viscous flow decrease with the increase in temperature in all these systems. This can be attributed to the effect of intermolecular interactions becoming weaker at higher temperature due to the decrease in the interaction strength of

intermolecular hydrogen bonding between the unlike molecules in the binary liquid mixtures

Deviation in viscosities $\Delta\eta$ values are positive for 3-chloroaniline with bromobenzene, chlorobenzene and nitrobenzene over the entire composition range at $T = (303.15 - 318.15)$ K. The positive data for all the binary systems suggests that the viscosity of the mixtures is higher than that of the pure components and hence, the fluidity of the mixture is low. This indicates the presence of specific interactions such as the formation of charge-transfer complexes between unlike molecules. The positive values of deviation in viscosity increase with increasing temperature for all the binary systems. The viscosity deviation values are found to be opposite to the sign of excess molar volumes for all binary mixtures, which is in agreement with the view proposed by Brocos et al.

The excess Gibbs energy of activation of viscous flow for three binary systems viz., 3-chloroaniline with bromobenzene, chlorobenzene and nitrobenzene, are positive over the entire composition range at all investigated temperatures. The positive values suggest that the dipole-induced interactions between the components of the mixtures are resulting in the formation of electron donor-acceptor complexes.

The variation of V^E , κ_s^E and $\Delta\eta$ with mole fraction are found to be fitted to the Redlich - Kister polynomial equation:

$$Y^E = x_1 x_2 \sum_{i=0}^j A_i (1 - 2x_1)^i$$

Where Y^E is the V^E or κ_s^E or $\Delta\eta$. The values of coefficients, A_i have been evaluated by using the least squares method. The standard deviation $\sigma(Y^E)$ are calculated by applying the following formula

$$\sigma(Y^E) = [\Sigma(Y_{exp}^E - Y_{cal}^E)^2 / (m-n)]^{1/2}$$

Where m is the total number of experimental points and n is the number of coefficients.

LIST OF PUBLICATIONS:

The research findings in the present work have been published in the following four Elsevier Journals:

1. P. Venkateswara Rao, T. S. Krishna, M. Gowri sankar, K. Ravindhranath, Excess molar volumes, speeds of sound and viscosities for binary mixtures of 3-chloroaniline with selected di- and tri- chlorosubstituted benzene at various temperatures- Comparison with Prigogine-Flory-Patterson theory, **Journal of Molecular Liquids, 222: 873-882 (2016) (Elsevier)**
2. P. Venkateswara Rao, M. Chandra Shekar, L. Venkatramana, M. Gowrisankar, K. Ravindhranath, Study of Intermolecular interactions in binary mixtures of 3-chloroaniline with isomeric chlorotoluenes at various temperatures, **Journal of Molecular Liquids, 219:289-298 (2016) (Elsevier)**
3. P. Venkateswara Rao, L. Venkatramana, M. Gowrisankar, K. Ravindranath, Volumetric, Acoustic and spectroscopic properties of 3-chloroaniline with substituted ethanols at various temperatures, **Journal of Chemical Thermodynamics, 94:186-196 (2016) (Elsevier)**
4. P. Venkateswara Rao, M. Gowrisankar, L. Venkatramana, K. Ravindhranath, Studies on the Importance of nature of substituent on the thermodynamic and transport properties of liquid mixtures at various temperatures, **Journal of Chemical Thermodynamics, 101:92-102 (2016) (Elsevier)**