Thermodynamic study of interactions in binary liquid mixtures of 2-Chloroaniline with some carboxylic acids

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ABSTRACT

Densities, speed of sound and dynamic viscosity of liquid mixtures of 2-Chloroaniline with carboxylic acids (ethanoic acid, propanoic acid and butanoic acid) have been calculated over the entire composition range and at $T = (303.15–318.15)$ K. Changes in the physical properties have been studied as a function of temperature and alkyl chain length of carboxylic acids. By using density, speed of sound, viscosity data the excess molar volume ($V^e_m$), excess isentropic compressibility ($κ^e_s$), excess Gibbs energy of activation flow ($ΔG^e/C^3$) of liquid mixtures have been calculated. In addition, excess partial molar volume, $V^e_{o,m}$; $1$, $V^e_{o,m}$; $2$; excess partial isentropic compressibility, $κ^e_{o,s}; m$; $1$, $κ^e_{o,s}; m$; $2$ at infinite dilution over the whole composition range have also been calculated. Further the topology of electron density obtained by non-covalent interaction plots are used to identify the evolution of strong and weak interactions between dimers of binary liquid mixtures.

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1. Introduction

Thermodynamic and transport property data are of great interest in process design and operation. Density, speed of sound and viscosity data are required in many chemical engineering calculations involving fluid flow, heat and mass transfer. The study of thermodynamic properties of binary liquid solution and their deviation from the ideality is found to be an excellent way to obtain the information about molecular structures and intermolecular interactions in liquid mixtures.[1–3]

In the present study, the binary liquid mixtures play a very important role industrially.

2-Chloroaniline is used in agricultural, pharmaceutical, rubber chemicals and as a parent substance in the production of antioxidants. It is also used in the manufacturing of synthetic dyes and organic pigments especially for red colour. Carboxylic acids are used in ink, pesticides, cosmetics, plastics and rubber as a chemical constituent. They are also important in industrial applications of compounds with carboxyl groups in the use of fatty acids in making soaps, detergents and shampoos.[4–8]

The present study is a continuation of our earlier research [9] on intermolecular interactions between 2-Chloroaniline and carboxylic acids. The aim of this study is to analyse the disruption of self-association in ethanoic acid, propanoic acid and butanoic acid, and breaking of dipole–dipole interaction of 2-Chloroaniline along with the interaction between $–NH_2$ group of 2-Chloroaniline and $–COOH$ group of carboxylic acids, respectively. In the present paper, we report densities ($ρ$),
speed of sound \((u)\) and viscosity \((\eta)\) of binary mixtures of 2-Chloroaniline with ethanoic acid, propanoic acid and butanoic acid including those of pure liquids at temperatures \((303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}\) and atmospheric pressure, covering the entire composition range expressed by the mole fraction \(x_1\) of 2-Chloroaniline.

The experimentally measured values of density, speed of sound and viscosity are used to compute the parameters, excess molar volume \((V^E_m)\), excess isentropic compressibility \((\kappa^E_s)\) and excess Gibbs energy of activation of viscous flow \((\Delta G^E_{C3})\) have been calculated. The partial molar volume \((\bar{V}^0_{m,1}, \bar{V}^0_{m,2})\), excess partial molar volume \((\bar{V}^{E}o_{m,1}, \bar{V}^{E}o_{m,2})\), excess partial molar volume at infinite dilution \((\bar{V}^{E}o_{m,\infty}, \bar{V}^{E}o_{m,\infty})\) and partial isentropic compressibility \((\bar{K}^0_{s,m,1}, \bar{K}^0_{s,m,2})\), excess partial isentropic compressibility \((\bar{K}^{E}o_{s,m,1}, \bar{K}^{E}o_{s,m,2})\), excess partial isentropic compressibility at infinite dilution \((\bar{K}^{E}o_{s,m,\infty}, \bar{K}^{E}o_{s,m,\infty})\) over the whole composition range has been calculated. The variations of all these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. These excess values are fitted to Redlich–Kister polynomial equation to estimate the binary coefficients and standard deviation between the experimental and calculated values. An extended analysis of the non-covalent interactions (NCI) was carried out to analyse the hydrogen bond interaction nature. The results are explained in terms of composition-dependent association behaviour in binary mixture.

2. Experimental

2.1. Materials

2-Chloroaniline of AR grade is procured from Sigma Aldrich, India. Carboxylic acids (AR grade) are procured from SD Fine Chemicals, India. All the chemicals are fractionally distilled and dried over 0.4 nm molecular sieves. The CAS Number, source, water content and mass fraction purity are given in Table 1. The purity of the chemicals is ascertained by comparing the experimental values of density, viscosity and speed of sound at temperatures \(T = (303.15-318.15) \text{ K}\) with the literature [10–17] (shown in Table 2).

2.2. Methods and measurements

The 2-Chloroaniline was procured from Sigma-Aldrich; carboxylic acids were procured from S.D. Fine Chemicals, India and purified by the fractional distillation method under reduced pressure. The water content was measured using Analab (Micro Aqua Cal 100) Karl Fischer Titrator and Karl Fisher reagent from Merck, by conductometric titration with dual platinum electrode. It can detect water content from less than 10 ppm to 100%. All the binary liquid mixtures are prepared by weighing appropriate amounts of pure liquids on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of \(\pm 0.00001 \text{ g}\), by syringing each component into airtight stopper bottles to minimise evaporation losses. The uncertainty in the estimation of mole fraction is \(\pm 1 \times 10^{-4}\).

| Table 1. Provenance, water content and mass fraction purity of the chemicals. |
|---------------------------------|----------------|---------------|---------------|---------------|
| Chemical name                  | CAS number    | Source        | Water content | Mass fraction purity | Mass fraction purity |
| 2-Chloroaniline                | 95-51-2       | Sigma Aldrich, India | 0.042    | 0.995 | 0.9960 |
| Ethanoic acid                  | 64-19-7       | S.D. Fine Chemicals, India | 0.040    | 0.995 | 0.9965 |
| Propanoic acid                 | 79-09-4       | S.D. Fine Chemicals, India | 0.038    | 0.995 | 0.9970 |
| Butanoic acid                  | 107-92-6      | S.D. Fine Chemicals, India | 0.041    | 0.995 | 0.9955 |
The density and speed of sound are measured with an Anton Paar (DSA 5000 M) instrument which employs the well-known oscillating U-tube principle (for density measurement). The instrument has a number of features for easy sample handling and to produce reliable results. It can measure the density in the range of 0 – 3 g cm\(^{-3}\) and speed of sound from 1000 to 2000 m·s\(^{-1}\), simultaneously at temperatures from 273.15 K to 343.15 K, with a pressure variation from 0 to 0.3 Mpa at low frequency (approximately 3 MHz). At regular intervals of time, the density meter is calibrated with dry air and millipore water as described in the manual. The samples are loaded into the density, speed of sound cell and the measurements are carried out by the slow equilibration mode, respectively. The values reported are the average of the three consecutive measurements carried out between the temperatures 303.15 and 318.15 K with an interval of 5 K under atmospheric pressure.

Dynamic viscosities are measured by Anton Paar microviscometer (Lovis 2000 ME) mounted on the master instrument DSA 5000 M. It can measure viscosity from 0.3 m Pa.s to 10,000 m Pa.s by rolling ball technique. The temperature is controlled by a built-in precise Peltier thermostat with an accuracy of 0.02 K. Before measurement, calibration is carried out using standard oils (S3, N26, N100 liquid for 1.59 mm, 1.8 mm and 2.5 mm capillary, respectively) provided by Anton Paar Co., Austria.

### 3. Computational details

Furthermore, for visualisation of NCI of dimers of 2-Chloroaniline and carboxylic acids, the reduced density gradient (RDG) \(s = 1/(2(3\pi^{2/3})p/p^{1/3})\) versus sign \(\lambda_2\) scattered graph associated with the hydrogen bonding regions in real space have been calculated using the Multiwfn program.[18] RDG method was recently proposed by Yang and co-workers,[19] which has been confirmed to be effective and convenient for identifying the NCI.
4. Results and discussion

The experimental values of densities, speed of sound and viscosity of the binary mixtures of 2-Chloroaniline with carboxylic acids, over the entire composition range, expressed in mole fraction, \( x_1 \) of 2-Chloroaniline at different temperatures are listed in Table 3, respectively.

4.1. Excess molar volume

The values of excess molar volumes \( V^E_m \) of binary mixtures of 2-Chloroaniline with carboxylic acids has been calculated from experimentally determined density data using the following equation:

\[
V^E_m = \left( \frac{x_1 M_1 + x_2 M_2}{\rho_{\text{mix}}} \right) - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right)
\]

where \( x_1, x_2, M_1, M_2, \rho_1 \) and \( \rho_2 \) are the mole fraction, molar weight and the density of pure component 1 and 2, respectively and \( \rho_{\text{mix}} \) is the measured density of the mixture and the data were given in Table 4. An examination of \( V^E_m \) data in the Figures 1–3 reveal that the property is negative at all temperatures over the entire composition range for the binary mixtures of 2-Chloroaniline with carboxylic acids.

The sign of \( V^E_m \) of binary systems depends upon the relative magnitude of expansion and contraction of mixing two liquids. When the factors causing expansion outweigh the factors causing contraction, \( V^E_m \) becomes positive. But if the contractive factors dominate over the expansive factors, \( V^E_m \) becomes negative.

The factors that are mainly responsible for volume expansion are:

(i) Breakdown of one or both components in solution system. A suitable example of this is the rupture of H-bonding of one compound by the other, or breaking up of associates held together by weaker physical forces, such as dipole–dipole or dipole–induced dipole interactions or by any other Vander Waals forces.

(ii) The geometry of molecular structure which does not favour fitting of the molecules with each other.

(iii) Steric hindrance which opposes the proximity of the constituent molecules.

The negative \( V^E_m \) arises due to dominance of the following factors:

(i) Chemical interaction between constituent molecules, such as heteromolecular association through the formation of H-bond, often termed as strong specific interaction.

(ii) Association through weaker physical forces, such as dipolar force or any other forces of this kind.

(iii) Accommodation of molecules of one component into the interstitials of the structural network of molecules of the other component.

(iv) Geometry of the molecular structure that favours fitting of the component molecules with each other.

The experimental results suggest that the contraction effect is dominant in the present investigation for all binary mixtures over the entire composition range at \( T = (303.15-318.15) \) K. An examination of data in the Table 4 suggests that the excess volume data for all binary systems are negative over the entire composition range at 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure.
Table 3. Density ($\rho$), viscosity ($\eta$) and speed of sound (u) of binary liquid mixtures of 2-Chloroaniline with carboxylic acids at temperatures $T = (303.15 \text{ to } 318.15)$ K.

| $x_1$     | $\rho$ (g/cm$^3$) | $\eta$ (m Pa.s) | u (m/s) |
|-----------|-------------------|-----------------|---------|
| 0.0000    | 1.0352            | 0.9766          | 1.014  |
| 0.1053    | 1.0349            | 0.9767          | 1.014  |
| 0.2106    | 1.0348            | 0.9768          | 1.014  |
| 0.3160    | 1.0347            | 0.9769          | 1.014  |
| 0.4213    | 1.0346            | 0.9770          | 1.014  |
| 0.5267    | 1.0345            | 0.9771          | 1.014  |
| 0.6321    | 1.0344            | 0.9772          | 1.014  |
| 0.7375    | 1.0343            | 0.9773          | 1.014  |
| 0.8429    | 1.0342            | 0.9774          | 1.014  |
| 0.9483    | 1.0341            | 0.9775          | 1.014  |
| 1.0537    | 1.0340            | 0.9776          | 1.014  |
| 2.0114    | 1.0339            | 0.9777          | 1.014  |
| 3.0690    | 1.0338            | 0.9778          | 1.014  |
| 4.1266    | 1.0337            | 0.9779          | 1.014  |
| 5.1842    | 1.0336            | 0.9780          | 1.014  |
| 6.2418    | 1.0335            | 0.9781          | 1.014  |
| 7.3023    | 1.0334            | 0.9782          | 1.014  |
| 8.3619    | 1.0333            | 0.9783          | 1.014  |
| 9.4215    | 1.0332            | 0.9784          | 1.014  |
| 10.4811   | 1.0331            | 0.9785          | 1.014  |

Standard uncertainties are $u(T) = 0.01$ K, $u(\rho) = \pm 0.0005$ g/cm$^3$, $u(\eta) = \pm 0.005$ m Pa.s, and $u(u) = \pm 0.08$ m/s (level of confidence 0.96).
Table 4. Excess molar volume ($V_m^e$), excess isentropic compressibility ($\kappa_f^e$), and excess Gibbs energy of activation flow ($\Delta G_f^{\text{act}}$) of binary liquid mixtures of 2-chloroaniline with carboxylic acids at temperatures $T$ (303.15–318.15) K.

| $\chi^1$ | $V_m^e$ (cm$^3$ mol$^{-1}$) | $\kappa_f^e$ (10$^6$ cm$^3$ mol$^{-1}$ K$^{-1}$) | $\Delta G_f^{\text{act}}$ (kJ mol$^{-1}$) |
|----------|---------------------------|-----------------------------------------------|-----------------------------------------|
| 0.1015   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.1941   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.1865   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.5242   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.5917   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.7564   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.8969   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 1.0105   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0684   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0953   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.1057   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0428   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0733   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.1118   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.1140   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.1171   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0113   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0115   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0118   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0140   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0142   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0154   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0159   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0165   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0171   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0176   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0180   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0185   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0190   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0195   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0200   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0205   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0210   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0215   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0220   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0225   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0230   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0235   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0240   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0245   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0250   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0255   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0260   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0265   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0270   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0275   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0280   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0285   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0290   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0295   | 0.0000                    | 0.0000                                        | 0.0000                                   |
| 0.0300   | 0.0000                    | 0.0000                                        | 0.0000                                   |
The algebraic values of $V^E_m$ for the binary mixtures of 3-Chloroaniline with carboxylic acids fall in the following order:

**Ethanoic acid < Propanoic acid < Butanoic acid**

According to these investigations, negative values of excess molar volumes of 2-Chloroaniline with carboxylic acids indicate that the changes of ‘free volume’ in the real mixtures and the presence of electron donor–acceptor interactions between carboxylic acids and 2-Chloroaniline (2-Chloroaniline behaves as an electron donor). In addition to the above effect, a dipole–dipole interaction between the carboxylic acid and amino group of 2-Chloroaniline also contributes to negative $V^E_m$ values.[20] A perusal of Table 4 shows that the $V^E_m$ values become more negative for 2-Chloroaniline with acetic acid mixture (Table 4) are attributed to the presence of strong specific interaction (hydrogen bonding between carbonyl group of carboxylic acid and hydrogen atom of amino group of 2-Chloroaniline) and also due to filling of smaller molecules into the voids created by bigger molecules of 2-Chloroaniline. The negative deviation of $V^E_m$ confirms the presence of strong molecular association in the system.[21]

Furthermore, in carboxylic acids a –COOH group has fixed power to release a proton because of electrometric and mesomeric effect of >C=O group. When the hydrogen atom of formic acid is replaced by an electron repelling alkyl group due to inductive effect (+I) the acidity of carboxylic acids can be rationalised by two electronegative oxygen atoms distorting the electron clouds surrounding the O–H bond, weakening it. The weak O–H bond causes the acid molecule to be less stable and causing hydrogen atom to be labile thus it dissociates easily to give proton (H$^+$). The acidic strength decreases as ethanoic acid > propanoic acid > butanoic acid due to +I effect of the increasing alkyl group. Owing to less acidity, hydrogen bond interactions are weaker in 2-Chloroaniline + butanoic acid and 2-Chloroaniline + propanoic acid mixtures thereby yielding less negative values of $V^E_m$ over the entire composition range.

A meticulous observation of Table 4 also shows that the $V^E_m$ values become more negative as the temperature is increased from 303.15 to 318.15 K. This indicates a gradually decreasing trend in the degree of the intermolecular hydrogen bonds in the associated 2-Chloroaniline molecules as the experimental temperature increases and dipole–dipole interactions between the hetero-molecules are increased leading to greater contraction in the mixture volumes.[22]

### 4.2. Excess partial molar volume

A more adventurous strategy to gain insight into the behaviour of various mixtures involves the generation of plots of partial excess molar volumes of the respective components

The partial molar volumes, $\nabla^o_{m,1}$ of component 1 (2-Chloroaniline ($x_1$)) and $\nabla^o_{m,2}$ of component 2 (carboxylic acids ($x_2$)) in the mixture over entire composition range are calculated using the following relations

$$
\nabla^o_{m,1} = V^E_m + V^e_{m,1} + x_2 \left( \frac{\partial V^E_m}{\partial x_1} \right)_{T,P} \tag{2}
$$

$$
\nabla^o_{m,2} = V^E_m + V^e_{m,2} - x_1 \left( \frac{\partial V^E_m}{\partial x_1} \right)_{T,P} \tag{3}
$$

where $V^e_{m,1}$ and $V^e_{m,2}$ are the molar volumes of pure components, 2-Chloroaniline and ethanoic acid, propanoic acid and butanoic acid. The derivative of $\left( \frac{\partial V^E_m}{\partial x_1} \right)$ in Equations (2)-(3) was obtained by differentiating Equation (27), which leads the following equations
The excess partial molar volumes $V_{m,1}^0$, $V_{m,2}^0$ over the whole composition range were calculated by using the following relations [23]

$$V_{m,1}^0 = V_{m,1}^* + x_2^n \sum_{i=0}^{n} A_i (1 - 2x_1)^i - 2x_1 x_2^n \sum_{i=1}^{n} A_i (1 - 2x_1)^{i-1}$$

(4)

$$V_{m,2}^0 = V_{m,2}^* + x_1^n \sum_{i=0}^{n} A_i (1 - 2x_1)^i + 2x_1 x_2^n \sum_{i=1}^{n} A_i (1 - 2x_1)^{i-1}.$$  

(5)

The values of excess partial molar volumes ($V_{m,1}^{0,E}$, $V_{m,2}^{0,E}$) are listed in Table S1. The excess partial molar volumes $V_{m,i}^{0,E}$ of 2-Chloroaniline and carboxylic acids at 303.15 K are shown in Figure 4. The excess partial molar volumes were calculated by subtracting the pure components molar volumes $V_{m,1}^*$ and $V_{m,2}^*$ from the right-hand sides of Equations (4) and (5). The negative excess partial molar volumes may be indicative of solute–solvent [24,25] interactions between unlike molecules, whereas positive values indicate the presence of strong self-association between like molecules. The observed excess partial molar volume value indicates cross-associations are strong compared to self-associations in 2-Chloroaniline and carboxylic acids. Another important property describing solution properties are the partial molar volumes of solution at infinite dilution. By setting $x_2 = 1$ in Equation (4), we get partial molar volumes of carboxylic acids at infinite dilution in 2-Chloroaniline

$$V_{m,1}^{0,\infty} = V_{m,1}^* + \sum_{i=0}^{n} A_i.$$  

(8)

![Figure 1](image_url). Excess molar volume ($V_m^E$) against mole fraction ($x_1$) for 2-Chloroaniline + Ethanoic acid at temperatures $T = (303.15–318.15)$ K.
Equally, by putting $x_2 = 0$ in Equation (5), gives an equation for the get partial molar volumes of 2-Chloroaniline at infinite dilution in carboxylic acids.

**Figure 2.** Excess molar volume ($V_m^E$) against mole fraction ($x_1$) for 2-Chloroaniline + Propanoic acid at temperatures $T = (303.15–318.15)$ K.

**Figure 3.** Excess molar volume ($V_m^E$) against mole fraction ($x_1$) for 2-Chloroaniline + Butanoic acid at temperatures $T = (303.15–318.15)$ K.
The excess partial molar volumes of at infinite dilution were calculated by

\[ V_{0,m}^{E,1} = \frac{V_{0,m}^{0}}{C_{m}^{1}} + \frac{V_{0,m}^{0}}{C_{m}^{2}} + \sum_{i=0}^{n} A_i (-1)^{n-1} \]

The excess partial molar volumes of at infinite dilution were calculated by

\[ V_{0,m,1}^{E,\infty} = V_{m,1}^{\infty} - V_{m,1}^{0} \]

\[ V_{0,m,2}^{E,\infty} = V_{m,2}^{\infty} - V_{m,2}^{0} \]

The values of excess partial molar volume of at infinite dilution \( V_{m,1}^{E,\infty} \), \( V_{m,2}^{E,\infty} \) for the selected binary systems at different temperatures are presented in Table 5. Most negative values of \( V_{m,1}^{E,\infty} \), \( V_{m,2}^{E,\infty} \) of 2-Chloroaniline + carboxylic acids shows stronger solute–solvent interactions at infinite dilution.

**Table 5.** The values of \( V_{m,1}^{E,\infty} \), \( V_{m,1}^{0} \), \( V_{m,2}^{E,\infty} \), \( V_{m,2}^{0} \) of the components for 2-Chloroaniline + carboxylic acid binary solutions at temperatures 303.15–318.15 K.

| T/K   | \( V_{m,1}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,1}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) |
|-------|-------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 303.15 | 105.411                             | 106.071                              | 57.540                              | 57.834                              |
| 308.15 | 105.753                             | 106.484                              | 57.690                              | 58.162                              |
| 313.15 | 106.125                             | 106.930                              | 57.942                              | 58.464                              |
| 318.15 | 106.347                             | 107.338                              | 58.108                              | 58.780                              |

2-Chloroaniline + Ethanoic acid

| T/K   | \( V_{m,1}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,1}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) |
|-------|-------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 303.15 | 105.569                             | 106.078                              | 74.990                              | 75.331                              |
| 308.15 | 105.900                             | 106.484                              | 75.328                              | 75.750                              |
| 313.15 | 106.259                             | 106.930                              | 75.660                              | 76.168                              |
| 318.15 | 106.582                             | 107.338                              | 76.008                              | 76.615                              |

2-Chloroaniline + Propanoic acid

| T/K   | \( V_{m,1}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,1}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) |
|-------|-------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 303.15 | 105.624                             | 106.071                              | 92.692                              | 92.951                              |
| 308.15 | 105.958                             | 106.484                              | 93.164                              | 93.443                              |
| 313.15 | 106.235                             | 106.930                              | 93.539                              | 93.942                              |
| 318.15 | 106.564                             | 107.338                              | 93.835                              | 94.341                              |

2-Chloroaniline + Butanoic acid

| T/K   | \( V_{m,1}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,1}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{0} \)/cm\(^3\).mol\(^{-1}\) | \( V_{m,2}^{E,\infty} \)/cm\(^3\).mol\(^{-1}\) |
|-------|-------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 303.15 | 105.624                             | 106.071                              | 92.692                              | 92.951                              |
| 308.15 | 105.958                             | 106.484                              | 93.164                              | 93.443                              |
| 313.15 | 106.235                             | 106.930                              | 93.539                              | 93.942                              |
| 318.15 | 106.564                             | 107.338                              | 93.835                              | 94.341                              |
4.3. Excess isentropic compressibility

The measurement of ultrasonic velocity, in combination with density, enables the accurate determination of molar isentropic compressibility and its partial value, which can be used to provide information about the nature of the interaction operating in the mixtures.

The isentropic compressibility is calculated by using the following comp

\[ \kappa_s = \frac{1}{\rho U^2}. \]  \hspace{1cm} (12)

Excess isentropic compressibilities were obtained by subtracting from \( \kappa_s \), the isentropic compressibility \( \kappa_{id} \) for the corresponding ideal mixture.

\[ k^E_s = k_s - k_{id} \]  \hspace{1cm} (13)

It can be shown that

\[ \kappa_{id} = \phi_1 \kappa_{s,1} + \phi_2 \kappa_{s,2} + T \left[ \frac{\phi_1 V_{m,1} (\alpha_{p,1})^2}{C_{p,1}} + \frac{\phi_2 V_{m,2} (\alpha_{p,2})^2}{C_{p,2}} - \frac{V_{m}^{id} (\alpha_{p}^{id})^2}{C_{p}^{id}} \right]. \]  \hspace{1cm} (14)

The molar heat capacity \( C_p \) values of pure components are determined by group contribution method [26] and from the experimental density results, the isobaric coefficient of thermal expansion can be calculated from the following equation,[27]

\[ \alpha = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P. \]  \hspace{1cm} (15)

The values \( k^E_s \) of were fitted with a polynomial expression similar to Equation (2). The coefficient and standard errors for these representations are listed Table 7.

Excess isentropic compressibility (\( k^E_s \)) data for the mixtures of 2-Chloroaniline with carboxylic acids were graphically depicted in Figures 5, 6 and 7 and the data were given in Table 4. An examination of data in the Table 4 suggests that the excess isentropic compressibility (\( k^E_s \)) data for all the binary systems are negative over the entire composition range at 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure.

Kiyohara and Benson [28] have suggested that \( k^E_s \) is the resultant of several opposing effects. A strong molecular interaction through hydrogen bonding, charge-transfer complex, dipole–dipole interactions, dipole–induced dipole interactions, interstitial accommodation and orientation ordering lead to a more compact structure making \( k^E_s \) negative and break-up of the carboxylic acid structures tend to make \( k^E_s \) positive.[29] The magnitude of the various contributions depends mainly on the relative molecular size of the components.

The algebraic values of \( k^E_s \) for the binary mixtures of 3-Chloroaniline with carboxylic acids fall in the following order:

Ethanoic acid < Propanoic acid < Butanoic acid.

The negative values of \( k^E_s \) suggest that the liquid mixture is less compressible than the pure liquids, indicating that the molecules in the mixture are more tightly bound than in pure liquids.

This corroborates the presence of relatively stronger molecular interaction, possibly through hydrogen bonding [30] between unlike molecules. It also suggests that decreasing dipole–dipole interaction due to decreasing proton donating ability with increasing chain length of alkyl group of carboxylic acid molecules.
Figure 5. Excess isentropic compressibility $\kappa^E_s$ against mole fraction ($x_1$) for 2-Chloroaniline + Ethanoic acid at temperatures $T = (303.15–318.15)$ K.

Figure 6. Excess isentropic compressibility $\kappa^E_s$ against mole fraction ($x_1$) for 2-Chloroaniline + s1 propanoic acid at temperatures $T = (303.15–318.15)$ K.
Examination curves in Figures 5–7 suggest that the chain length of alkyl group of carboxylic acid molecule increases, which in turn decreases the polarisability causing the decrease in $\kappa^E_s$ values. This observation is similar to that of the literature which was reported earlier by Garcia et al. [3] Ali and Nain [31] Ali et al. [32,33] and L.I.Welford-Abbzey et al.[34]

**4.4. Excess partial molar isentropic compressibility**

The partial molar isentropic compressibility $\kappa^0_{s,m,1}$ of 2-Chloroaniline and $\kappa^0_{s,m,2}$ of carboxylic acid mixtures over entire composition range were calculated by using the following relations.[35]

\[
\kappa^0_{s,m,1} = \kappa_2^* + \kappa_{s,m,1}^* + x_2 \left( \frac{\partial \kappa_2^*}{\partial x_1} \right)_{T,P}
\]

\[
\kappa^0_{s,m,2} = \kappa_2^* + \kappa_{s,m,2}^* - x_1 \left( \frac{\partial \kappa_2^*}{\partial x_1} \right)_{T,P}
\]

where $\kappa_{s,m,1}^*$ and $\kappa_{s,m,2}^*$ are the molar isentropic compressibility of pure components, 2-Chloroaniline and ethanoic acid, propanoic acid and butanoic acid. The derivative of $\left( \frac{\partial \kappa_2^*}{\partial x_1} \right)$ in Equations (16)-(17) was obtained by differentiating Equation (13), which leads the following equations

\[
\kappa^0_{s,m,1} = \kappa_{s,m,1}^* + x_2^2 \sum_{i=0}^{n} A_i(1 - 2x_1)^i - 2x_1 x_2^2 \sum_{i=1}^{n} A_i(1 - 2x_1)^{i-1}
\]
\[ 3 \text{m} \frac{\text{TPa}}{\text{mol}^{1/2}} \]

The excess partial molar isentropic compressibility \( \kappa^E \) over the whole composition range were calculated by using the following relations

\[ \kappa^E_{s,m_1} = \kappa^E_{s,m_2} = \kappa^E_{s,m_1} - \kappa^E_{s,m_1} \]

The values of partial and excess partial molar isentropic compressibilities \( \kappa^0_{s,m_1}, \kappa^0_{s,m_2}, \kappa^0_{s,m_1} \) are listed in Table S2. The variation of excess partial molar isentropic compressibilities \( \kappa^E_{s,m_1}, \kappa^E_{s,m_2} \) with composition at 303.15 K are presented in Figure 8. We note that all of the molar isentropic compressions of each component in the mixture are less than their respective molar isentropic compressions in the pure state, that is, there is a decrease in the molar isentropic compression on mixing 2-Chloroaniline with carboxylic acids. It is also observed from Table S2 negative values of \( \kappa^E_{s,m_1}, \kappa^E_{s,m_2} \) of both components of the mixtures at each temperature. The negative values of \( \kappa^E_{s,m_1}, \kappa^E_{s,m_2} \) are higher in the mixture with ethanoic acid that with 2-Chloroaniline. This supports the presence of strong intermolecular interactions between unlike molecules and more pronounced interactions in the mixtures of 2-Chloroaniline with carboxylic acids.

The partial molar isentropic compressibility of 2-Chloroaniline at infinite dilution \( \kappa_{s,m_1} = 1 \) in carboxylic acids, and the partial molar isentropic compressibilities of carboxylic acids at infinite dilution \( \kappa_{s,m_2} = 1 \) in 2-Chloroaniline. Therefore, \( \kappa^0_{s,m_1} \) is obtained by setting \( x_2 = 0 \) in Equation (18) which leads to

\[ \kappa^0_{s,m_1} = \kappa^s_{s,m_2} + \sum_{n=1}^{\infty} A_n. \]

Similarly, setting \( x_2 = 0 \), leads to in Equation (19)

\[ \kappa^0_{s,m_2} = \kappa^s_{s,m_1} + \sum_{n=1}^{\infty} A_n (-1)^{n-1}. \]

Figure 8. Variation of excess partial molar isentropic compressibility \( \kappa^E_{s,m_1}, \kappa^E_{s,m_2} \) of (a) 2-Chloroaniline and (b) carboxylic acids (ethanoic acid, propanoic acid, butanoic acid), respectively, against mole fraction, \( x_1 \) of 2-Chloroaniline for the binary mixtures of at \( T = 303.15 \) K. (■) - 2-Chloroaniline + Ethanoic acid, (●) - 2-Chloroaniline + Propanoic acid, (▲) - 2-Chloroaniline + Butanoic acid.
Excess partial molar isentropic compressibility $K_{s,m,1}^{\theta E}$, $K_{s,m,2}^{\theta E}$ at infinite dilution for each component in the binary mixtures are evaluated by using the following relations

$$K_{s,m,1}^{\theta E} = K_{s,m,1}^{0,\infty} - K_{s,m,1}^s,$$

$$K_{s,m,2}^{\theta E} = K_{s,m,2}^{0,\infty} - K_{s,m,2}^s.$$

The values of partial molar isentropic compressibility and excess partial molar isentropic compressibility at carboxylic acids are $(K_{s,m,1}^s, K_{s,m,2}^s, K_{s,m,1}^{0,\infty}, K_{s,m,2}^{0,\infty})$ reported in Table 6. It is observed from Table 6 that the partial molar isentropic compressibility of 2-Chloroaniline at infinite dilution $K_{s,m,1}^{\theta E}$ in carboxylic acids and carboxylic acids at infinite dilution $K_{s,m,2}^{\theta E}$ in 2-Chloroaniline are smaller than the corresponding molar compressibilities $K_{s,m,1}^s, K_{s,m,2}^s$ of 2-Chloroaniline and carboxylic acids. The values are negative in general, for all the studied systems with some exceptions indicating strong solute–solvent interactions which results in less compressible solutions.

4.5. Excess Gibbs energy of activation of viscous flow

The excess Gibbs energy of activation of viscous flow is calculated from the following relation,[36]

$$\Delta G^{\ast E} = RT \left[ \ln(V\eta) - \sum_{i=1}^{N} x_i \ln(V_i\eta_i) \right].$$

(26)

where $V$ and $\eta$ are the molar volume and dynamic viscosity of the mixtures, respectively, and $x_i, V_i$ and $\eta_i$ are the mole fraction, molar volume and dynamic viscosity of the pure components, respectively. $R$ is the gas constant and $T$ is the absolute temperature.

The excess Gibbs energy of activation of viscous flow for the all binary systems is presented in Table 4. The values of the $\Delta G^{\ast E}$ are positive for all the binary systems gives information regarding the presence of strong interaction between unlike molecules in solvent mixtures as suggests by Oswal and Desai.[2] This supports the view that chemical interaction which may involve association due to hydrogen bonding, dipole–dipole interaction, formation of complexes due to charge transfer may lead to strong interactions. Prolongo et al.[37] have observed the correlation between the sign of $V_m^{\theta E}$ and $\Delta G^{\ast E}$ in a number of systems, $\Delta G^{\ast E}$ being positive when $V_m^{\theta E}$ is negative. All of the three of binary mixture support this conjecture.

All the excess values are fitted by the method of non-linear least-squares to a Redlich–Kister[38] polynomial equation of the type,

$$Y^E = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i.$$

(27)

where $x_1$ is the mole fraction of 2-Chloroaniline and $x_2$ is the mole fraction of carboxylic acids and the subscription $i$ in the equation takes the values from 0 to 2. The values of $A_i$ are the binary coefficients obtained by the method of least squares.

The standard deviation ($\sigma$) is calculated using the relation,

$$\sigma = \left[ \frac{\sum (Y_{\text{exp}}^{E} - Y_{\text{cal}}^{E})^2}{N - n} \right]^{\frac{1}{2}}.$$

(28)
Table 6. The values of $K^0_{1,m,1}$, $K^*_{1,m,1}$, $K^0E_{1,m,1}$, $K^0_{1,m,2}$, $K^*_1$, $K^0_{1,m,2}$ of the components for 2-Chloroaniline + carboxylic acid binary solutions at temperatures 303.15–318.15 K.

| T/K   | $K^0_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^*_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^0E_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^0_{1,m,2}/m^3$.N$^{-1}.mol^{-1}$ | $K^*_{1,m,2}/m^3.TPa^{-1}.mol^{-1}$ | $K^0E_{1,m,2}/m^3.TPa^{-1}.mol^{-1}$ |
|-------|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|
| 303.15| 2.3350                              | 4.0842                              | -1.7492                             | 3.4730                            | 4.4602                              | -0.9872                             |
| 308.15| 2.0493                              | 4.2083                              | -2.1590                             | 3.1791                            | 4.6354                              | -1.4563                             |
| 313.15| 1.7974                              | 4.3514                              | -2.5590                             | 2.9847                            | 4.8405                              | -1.8558                             |
| 318.15| 1.3928                              | 4.4859                              | -3.0931                             | 2.5311                            | 5.0556                              | -2.5245                             |

2-Chloroaniline + Ethanoic acid

| T/K   | $K^0_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^*_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^0E_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^0_{1,m,2}/m^3$.N$^{-1}.mol^{-1}$ | $K^*_{1,m,2}/m^3.TPa^{-1}.mol^{-1}$ | $K^0E_{1,m,2}/m^3.TPa^{-1}.mol^{-1}$ |
|-------|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|
| 303.15| 2.9761                              | 4.0848                              | -1.1087                             | 5.5134                            | 6.0266                              | -0.5132                             |
| 308.15| 2.5103                              | 4.2083                              | -1.6980                             | 5.4153                            | 6.3079                              | -0.8926                             |
| 313.15| 2.1036                              | 4.3514                              | -2.2478                             | 5.3787                            | 6.5938                              | -1.2150                             |
| 318.15| 1.7849                              | 4.4859                              | -2.7011                             | 5.3822                            | 6.8986                              | -1.5164                             |

2-Chloroaniline + Propanoic acid

| T/K   | $K^0_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^*_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^0E_{1,m,1}/m^3.TPa^{-1}.mol^{-1}$ | $K^0_{1,m,2}/m^3$.N$^{-1}.mol^{-1}$ | $K^*_{1,m,2}/m^3.TPa^{-1}.mol^{-1}$ | $K^0E_{1,m,2}/m^3.TPa^{-1}.mol^{-1}$ |
|-------|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|
| 303.15| 3.5917                              | 4.0842                              | -0.4924                             | 6.9030                            | 7.2999                              | -0.3969                             |
| 308.15| 3.3843                              | 4.2083                              | -0.8240                             | 7.1111                            | 7.6240                              | -0.5129                             |
| 313.15| 2.9206                              | 4.3514                              | -1.4308                             | 7.1943                            | 7.9562                              | -0.7619                             |
| 318.15| 2.2572                              | 4.4859                              | -2.2287                             | 7.1867                            | 8.2923                              | -1.1056                             |

2-Chloroaniline + Butanoic acid
where $N$ represents the number of experimental points and $n$ represents the number of coefficients.

Table 7 shows the values of adjustable parameters and standard deviations of Redlich–Kister polynomial equations. The values of standard deviations are giving satisfactory results for the experimental values.

### 4.6. Non-covalent interaction (NCI) plots

Moreover, a perusal of the non-covalent intermolecular interactions proposed by Yang and co-worker,[19] indicates the plots in Figure 9 the RDG versus sign ($\lambda_2$) and the RDG isosurface with $s = 0.50$ a.u. of the three associations are operative the typical character of sharp spike(s) of weak intermolecular interactions in the low-density region of component molecules. They are different cross-associated dimers are possible in which O-H...N

| Binary mixtures                  | Functions | $A_0$       | $A_1$       | $A_2$       | $A_3$       | $A_4$       | $\sigma$   |
|----------------------------------|-----------|-------------|-------------|-------------|-------------|-------------|------------|
|                                  |           | $T = 303.15$ K |             |             |             |             |            |
| 2-Chloroaniline + Ethanoic acid  | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4506 | -0.0936 | -0.0482 | -0.0306 | -0.0585 | 0.0006     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -207.894 | -94.464 | -51.8543 | 8.048092 | 82.93627 | 0.3037     |
|                                  | $k_i$ / TPa$^{-1}$ | 34.9959 | 15.7532 | 9.3384 | 3.2523 | -1.4661 | 0.0105     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | -140.191 | 48.2014 | -2.9420 | -6.0413 | 33.7806 | 0.1979     |
| 2-Chloroaniline + Propanoic acid | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4268 | -0.1152 | 0.0109 | 0.0352 | -0.0054 | 0.0002     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -116.212 | 20.1554 | 56.6883 | 11.7371 | 2.7140 | 0.2987     |
|                                  | $k_i$ / TPa$^{-1}$ | 32.4761 | 14.1083 | 4.8129 | 3.2824 | 2.2857 | 0.0056     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | 20.2760 | 8.7215 | 1.6995 | -0.3050 | -0.9460 | 0.0049     |
|                                  | $T = 308.15$ K |             |             |             |             |             |            |
| 2-Chloroaniline + Ethanoic acid  | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4758 | -0.0860 | -0.1189 | -0.0435 | -0.0065 | 0.0008     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -223.882 | -102.061 | -59.3739 | -6.93106 | 36.59956 | 0.3021     |
|                                  | $k_i$ / TPa$^{-1}$ | 36.0185 | 16.1968 | 10.5229 | 2.9899 | 11.0271 | 0.0233     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | 33.1466 | 14.4027 | 5.2845 | 3.2620 | 3.4003 | 0.0051     |
| 2-Chloroaniline + Propanoic acid | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4476 | -0.0978 | -0.0929 | 0.0193 | 0.0540 | 0.0005     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -166.015 | -55.5856 | -9.1538 | 34.7540 | -37.8454 | 0.1014     |
|                                  | $k_i$ / TPa$^{-1}$ | 33.1466 | 14.4027 | 5.2845 | 3.2620 | 3.4003 | 0.0052     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | 103.763 | 26.9604 | 17.9178 | 6.93106 | 36.59956 | 0.3021     |
|                                  | $T = 313.15$ K |             |             |             |             |             |            |
| 2-chloroaniline + Ethanoic acid  | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4998 | -0.0792 | -0.1813 | -0.0618 | 0.0175 | 0.0002     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -223.882 | -102.061 | -59.3739 | -6.93106 | 36.59956 | 0.3021     |
|                                  | $k_i$ / TPa$^{-1}$ | 36.5808 | 16.4506 | 10.6723 | 3.0264 | 1.1127 | 0.0024     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | 36.5808 | 16.4506 | 10.6723 | 3.0264 | 1.1127 | 0.0024     |
| 2-chloroaniline + Propanoic acid | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4653 | -0.0887 | -0.1712 | 0.0045 | 0.0523 | 0.0006     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -166.015 | -55.5856 | -9.1538 | 34.7540 | -37.8454 | 0.1014     |
|                                  | $k_i$ / TPa$^{-1}$ | 33.1466 | 14.4027 | 5.2845 | 3.2620 | 3.4003 | 0.0051     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | 139.477 | 30.9337 | 29.1308 | -9.1175 | -11.2570 | 0.3507     |
|                                  | $T = 318.15$ K |             |             |             |             |             |            |
| 2-chloroaniline + Ethanoic acid  | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.0723 | -0.1627 | -0.0882 | -0.1395 | -0.1395 | 0.0005     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -260.106 | -124.127 | -95.7125 | -26.9604 | -35.7883 | 0.2123     |
|                                  | $k_i$ / TPa$^{-1}$ | 37.2405 | 16.2589 | 11.4996 | 4.9438 | 5.4147 | 0.0019     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | -173.461 | -32.7108 | -12.1459 | -103.763 | -92.12 | 0.5577     |
| 2-chloroaniline + Propanoic acid | $V_p^1$ / cm$^3$.mol$^{-1}$ | -0.4843 | -0.0832 | -0.2030 | 0.0097 | 0.0048 | 0.0008     |
|                                  | $\tilde{V}_p^1$ / cm$^3$.mol$^{-1}$ | -36.1566 | 16.3856 | 8.7519 | 2.7847 | 3.4461 | 0.0021     |
|                                  | $k_i$ / TPa$^{-1}$ | -152.803 | 37.0597 | 25.7684 | -28.1444 | -52.1835 | 0.2881     |
|                                  | $\Delta G^E / 2J$.mol$^{-1}$ | 26.8422 | 11.8065 | 2.9338 | 2.6130 | 5.4950 | 0.0016     |
hydrogen bonds shows stronger interaction [9] compared to remaining hydrogen bond interactions.

The possible O-H...N cross-associated dimers are shown in the Figure 10.

In the case of dimer I, II and III, two low-reduced gradient spikes at low density now lies at negative values of −0.03468 and −0.01422 a.u., respectively, indicative of a stabilising hydrogen bond interaction. For dimer III, the spikes very near zero, indicating weak hydrogen bond interactions (−0.01422 a.u.). So the stability order of the dimers was I > II > III which is in agreement with the thermodynamic results. Apart from this, the RDG isosurfaces reveal a productive visualisation of NCI as the broad regions in real space. For three associations employed, it is possible to obtain the strong H-bonds, weaker H-bonds and weaker repulsive interactions accordingly on the gradient isosurfaces. Resultant plots reveal that, as anticipated, a blue bonding isosurface lies between hydrogen donor of hydroxyl group of carboxylic acids and nitrogen acceptor of 2-Chloroaniline, is the characteristic sign of strong hydrogen H-bond, and a green bonding isosurface indicated Vander Waals interaction. Simultaneously a red non-bonded overlap isosurface appears between the two monomers and centre of rings shows intermolecular weak steric repulsive interaction. The overall result of the gradient isosurface plot analysis is completely consistent with that of the scatter diagram.

Figure 9. Plots of the reduced density gradient(s) v.s. the electron density multiplied by the sign of the second Hessian eigenvalue (λ2) and gradient of isosurfaces with s = 0.5 a.u. for the three hydrogen bond associations. (I) 2-Chloroaniline + Ethanoic acid (II) 2-Chloroaniline + Propanoic acid (III) 2-Chloroaniline + Butanoic acid.
Finally, an examination of the gradient isosurfaces, the intermolecular dispersion interactions of the cross-associations are larger in 2-Chloroaniline and ethanoic acid than the 2-Chloroaniline when compared with propanoic acid and butanoic acids.

5. Conclusions

In this work, we have presented the observed values of density, speed of sound and viscosity are reported for binary mixtures of 2-Chloroaniline with carboxylic acids over the entire range of mole fraction at $T = (303.15–318.15)$ K. Calculated excess values of 2-Chloroaniline/carboxylic acids mixture shows strong deviations from ideality because of the existence of strong hetero-associations competing with homoassociations through H-bonding. Further the NCI plots are performed on intermolecular associations to deepen the nature of the intermolecular associated interaction. The NCI plot analysis was in good agreement with the results of the experimental determination.
Figure 9. Continued.

Figure 10. Optimised N–H…O hydrogen-bonded structures of (I) 2-Chloroaniline + Ethanoic acid (II) 2-Chloroaniline + Propanoic acid (III) 2-Chloroaniline + Butanoic acid.
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