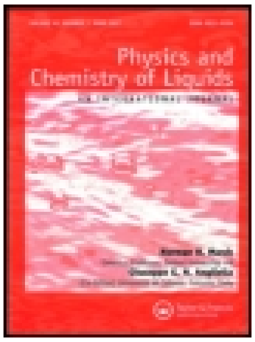

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# A thermodynamic and density functional theory study of intermolecular interactions between 2-methylaniline and some alkyl acrylates

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**ABSTRACT**
The densities ($\rho$) and speeds of sound ($u$) are reported for binary mixtures of 2-methylaniline with methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA), over the entire composition range from 303.15 K to 318.15 K and at atmospheric pressure 0.1 MPa. The excess functions ($V^E$ and $\kappa_s^E$) are calculated from the densities and speeds of sound at experimental temperatures. Excess functions are correlated by the Redlich – Kister equation. Quantum mechanical approach was used to study the intermolecular hydrogen bond interactions in self and cross-associated complexes of 2-methylaniline and alkyl acrylate with the aid of DFT in the gas phase.

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**KEYWORDS**
2-methylaniline; alkyl acrylate; DFT; NBO; interaction energy

## Introduction

The molecular interactions at microscopic levels will reflect and alter the bulk properties. Hence, a thorough understanding of the nature and strength of molecular forces existing between molecule to molecule in pure liquids and in their blends and their variations with respect to various physicochemical parameters, is essential because the organic solvents are indispensable components of any industry.

The success or failure of quantification of industrial products of compounds is originated from the binding forces envisaged in and/or by the clusters of molecules at micro levels. To peep into the forces operating at molecular levels, thermodynamic is the only answer. The determination of various thermodynamic parameters and their variations pertaining to organic solvents and their blends, and correlating the observed data from the view point of structure of the molecules, will be of immense help for an Scientists/engineers to optimise the design parameters for the manufacturing the product.

Our research group is investigating on these aspects of research with respect to binary liquid mixtures and some of the novel findings are reported to the literate [1–4]. In the present work, binary blends of 2-methylaniline with some alkyl acrylates viz., methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA), have been investigated.

In the present study, the liquids have been chosen on the basis of their industrial importance. O-toluidine is chosen as a polar solvent and self-associated through hydrogen bonding of its amine group. The amino group in o-toluidine is an electron donor and also plays the role of proton-acceptor centre and the alcohol molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups. O-toluidine is an important compound used in the manufacturing of dyes and of rubber vulcanisation accelerators. It is also used in the fabrication of hypnotic and anaesthetic

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pharmaceuticals and pesticides [5] whereas acrylate monomers are often required for their industrial applications such as in making cleaning products, antioxidant agents, amphoteric surfactants, paints, inks, adhesives, dispersions for textiles, paper, etc., and are also interesting theoretically as they have unsaturated structure along side of a carbonyl group in the molecule [6–9].

The present study was undertaken to determine experimentally the density and speed of sound of pure liquids of methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) and their binary mixtures with 2-methylaniline at temperature (T) of 303.15–318.15 K. In the theoretical study, the geometrical structures of monomers and all possible hydrogen-bonded dimers are fully optimised using the density functional theory (DFT) with the Lee–Yang–Parr (LYP) correlation function (B3LYP) and the 6–311++G(d,p) basis set. A comprehensive analysis of the computational results are carried out to confirm the hydrogen bond complex formation and to better explore the nature of the hydrogen-bond interaction.

## 2. Experimental and computational methods

### 2.1. Materials

2-methylaniline, methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) of analytic grade (Sigma Aldrich, India, purity >99.5%) were used without purification. The purity of chemicals was tested by comparing densities ($\rho$) and speed of sound ($u$) with literature values in the temperature range from 303.15 K to 318.15 K and are shown in Table 1. The experimental values are found to be in good agreement with the reported values [10–14].

**Table 1.** Comparison of experimental values of density ($\rho$) and speed of sound ($u$) of pure liquids with literature Values at temperatures $T$ = (303.15 to 318.15) K.

| | Density (g•cm$^{-3}$) | | Speed of sound (m•s$^{-1}$) | |
|---|---|---|---|---|
| Component | Experimental | Literature | Experimental | Literature |
| | | 2-methylaniline | | |
| 303.15 K | 0.99019 | 0.9902[a] | 1578.5 | 1579.0 [c] |
| 308.15 K | 0.98599 | 0.9860[b] | 1558.2 | 1558.3[b] |
| 313.15 K | 0.98169 | 0.9817 [c] | 1538.5 | 1539.0 [c] |
| 318.15 K | 0.97759 | - | 1520.5 | - |
| | | Methyl acrylates(MA) | | |
| 303.15 K | 0.94158 | 0.94340[d] | 1161.1 | 1162.2 [h] |
| 308.15 K | 0.93562 | 0.93560[e] | 1142.1 | 1139.1 [h] |
| 313.15 K | 0.92969 | 0.93054 [f] | 1123.8 | 1117.8 [h] |
| 318.15 K | 0.92373 | 0.92425 [f] | 1111.6 | 1095.7 [h] |
| | | Ethyl acrylates (EA) | | |
| 303.15 K | 0.91023 | 0.91031 [f] | 1144.10 | 1145.1[d] |
| 308.15 K | 0.90432 | 0.90448 [f] | 1110.41 | 1118.7[d] |
| 313.15 K | 0.89849 | 0.89862 [f] | 1089.63 | 1097.2[d] |
| 318.15 K | 0.89268 | 0.89273 [g] | 1081.70 | 1076.7[d] |
| | | Butyl acrylate (BA) | | |
| 303.15 K | 0.88935 | 0.88911 [f] | 1189.60 | 1185.38 [f] |
| 308.15 K | 0.88460 | 0.88411 [f] | 1171.10 | 1165.95 [f] |
| 313.15 K | 0.87985 | 0.87909 [f] | 1149.10 | 1146.68 [f] |
| 318.15 K | 0.89271 | 0.87406 [f] | 1128.60 | 1127.55 [f] |

[a]Ref. [10], [b] Ref [11]., [c] Ref [12]., [d] Ref [13]., [e] Ref [14]., [f] Ref [15]., [g] Ref [16]., [h] Ref [17].,

### 2.2. Measurements

Binary liquid mixtures of 2-methylaniline and alkyl acrylates were prepared in different compositions by weighing appropriate amounts of pure liquids on a digital electronic balance (MettlerToledo AB 135, Switzerland) with an uncertainty of ±0.00001 g. To minimise the evaporation or absorption losses, samples were kept in airtight-stoppered bottles. The uncertainty in mole fraction was found to be± $1 \times 10^{-4}$.

The values of density, $\rho$ and speed of sound, $u$ were measured with an Anton Paar (DSA 5000 M) vibrating u-tube densitometer, which is calibrated by using ultra pure distilled water and dry air at different temperatures and atmospheric pressure. The built in thermostat controls the temperature in the vibrating U-tube with a precision of ±0.01 K. The estimated uncertainties of measured density and speed of sound were, ±0.0004 g $cm^{-3}$and ±0.5 m $s^{-1}$ and for$V_m^E$,$k_s^E$with uncertainties ±0.007 $cm^3 \cdot mol^{-1}$, ±0.04 $TPa^{-1}$, respectively.

## 3. Computational methods

### 3.1 DFT calculations

Quantum mechanical electronic structure calculations are used to evaluate the intermolecular hydrogen bonding between 2-methylaniline and alkyl acrylate complexes. The geometrical parameters, interactions energies, second-order perturbation stabilisation energies and electron densities were calculated by using B3LYP method using basis set$6-311++G(d,p)$. All these simulations in the gas phase were carried out using Gaussian 09 software. Charge densities, Laplacian charge densities and total electron energy densities were computed by using Multiwfn program at bonding critical point (BCP). The non-covalent interactions (NCI) plots are employed for real-space visualisation of attractive interactions between 2-methylaniline and alkyl acrylate.

## 4. Results and discussion

The experimental measured values of density, speed of sound of the systems 2-methylaniline(2 MA) + methyl acrylate (MA), 2-methylaniline(2 MA) + ethyl acrylate (EA) and 2-methylaniline + 1 butyl acrylate (BA) have been measured at a temperature range 303.15–318.15 K and as a function of composition are listed in Table 2.

### 4.1. Excess properties

The values of excess molar volume of 2-methylaniline+ alkyl acrylate liquid mixtures were determined by using the following equation:

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right) \tag{1}$$

Where $x_i, M_i$ and $\rho_i$are the mole fraction, molar weight and density of i^th^ component of mixtures and $\rho$ is the density of the mixtures.

The isentropic compressibility ($\kappa_s$) as follows:

$$\kappa_s = \frac{1}{\rho . U^2} \tag{2}$$

The comparable excess isentropic compressibilities (${\kappa_s}^E$) have been calculated from the subsequent equation:

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{3}$$

**Table 2.** Density ($\rho$) and speed of sound ($u$) of binary liquid mixtures of 2-methylaniline with alkyl acrylates at temperatures $T$ = (303.15 to 318.15) K.

| | $\rho$/gm cm$^{-3}$ | | | | $u$/m s$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| $x_1$ | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| | | | | 2-methylaniline + methyl acrylates (MA) | | | | |
| 0.0000 | 0.94158 | 0.93562 | 0.92969 | 0.92373 | 1161.10 | 1142.10 | 1123.80 | 1111.60 |
| 0.0844 | 0.94681 | 0.94107 | 0.93536 | 0.92964 | 1186.15 | 1155.28 | 1141.16 | 1119.22 |
| 0.1717 | 0.95194 | 0.94638 | 0.94081 | 0.93525 | 1212.57 | 1174.24 | 1166.71 | 1144.45 |
| 0.2622 | 0.95698 | 0.95159 | 0.94618 | 0.94079 | 1241.51 | 1196.32 | 1194.90 | 1172.58 |
| 0.3560 | 0.96194 | 0.95671 | 0.95147 | 0.94626 | 1273.86 | 1222.69 | 1226.58 | 1204.34 |
| 0.4533 | 0.96685 | 0.96180 | 0.95670 | 0.95168 | 1310.06 | 1254.21 | 1262.53 | 1240.42 |
| 0.5543 | 0.97166 | 0.96678 | 0.96185 | 0.95703 | 1350.65 | 1292.08 | 1303.32 | 1281.41 |
| 0.6593 | 0.97637 | 0.97169 | 0.96694 | 0.96231 | 1396.43 | 1338.05 | 1349.87 | 1328.58 |
| 0.7683 | 0.98103 | 0.97654 | 0.97195 | 0.96752 | 1448.37 | 1394.70 | 1403.43 | 1383.00 |
| 0.8818 | 0.98564 | 0.98133 | 0.97692 | 0.97268 | 1508.31 | 1466.01 | 1465.73 | 1446.65 |
| 1.0000 | 0.99019 | 0.98599 | 0.98169 | 0.97759 | 1578.50 | 1558.20 | 1538.50 | 1520.50 |
| | | | | 2-methylaniline + ethyl acrylates (EA) | | | | |
| 0.0000 | 0.91023 | 0.90432 | 0.89849 | 0.89268 | 1144.10 | 1110.41 | 1089.63 | 1081.70 |
| 0.0998 | 0.91836 | 0.91269 | 0.90705 | 0.90146 | 1163.70 | 1118.91 | 1106.10 | 1096.94 |
| 0.1997 | 0.92652 | 0.92100 | 0.91551 | 0.93538 | 1186.55 | 1133.19 | 1128.59 | 1118.73 |
| 0.2996 | 0.93469 | 0.92933 | 0.92399 | 0.94103 | 1212.92 | 1151.67 | 1154.70 | 1144.26 |
| 0.3995 | 0.94279 | 0.93758 | 0.93236 | 0.94654 | 1243.60 | 1175.65 | 1185.57 | 1174.50 |
| 0.4995 | 0.95086 | 0.94581 | 0.94075 | 0.95200 | 1279.44 | 1206.30 | 1221.98 | 1210.21 |
| 0.5995 | 0.95880 | 0.95394 | 0.94904 | 0.95734 | 1321.02 | 1244.97 | 1264.71 | 1252.17 |
| 0.6996 | 0.96672 | 0.96205 | 0.95732 | 0.96260 | 1369.73 | 1294.34 | 1315.38 | 1302.00 |
| 0.7997 | 0.97460 | 0.97010 | 0.96553 | 0.96777 | 1427.14 | 1358.20 | 1376.05 | 1361.61 |
| 0.8998 | 0.98241 | 0.97808 | 0.97369 | 0.97281 | 1495.53 | 1442.53 | 1449.19 | 1433.57 |
| 1.0000 | 0.99019 | 0.98599 | 0.98169 | 0.97759 | 1578.50 | 1558.20 | 1538.50 | 1520.50 |
| | | | | 2-methylaniline + butyl acrylate (BA) | | | | |
| 0.0000 | 0.88935 | 0.88460 | 0.87985 | 0.89271 | 1189.60 | 1171.10 | 1149.10 | 1128.60 |
| 0.1271 | 0.89946 | 0.89481 | 0.89015 | 0.90153 | 1212.87 | 1191.94 | 1169.34 | 1150.46 |
| 0.2468 | 0.90963 | 0.90504 | 0.90042 | 0.93538 | 1238.46 | 1215.08 | 1191.76 | 1158.23 |
| 0.3597 | 0.91981 | 0.91527 | 0.91068 | 0.94105 | 1266.58 | 1240.99 | 1217.12 | 1186.35 |
| 0.4663 | 0.92997 | 0.92547 | 0.92093 | 0.94660 | 1297.58 | 1270.12 | 1245.83 | 1217.82 |
| 0.5672 | 0.94011 | 0.93566 | 0.93115 | 0.95207 | 1331.97 | 1303.18 | 1278.70 | 1253.28 |
| 0.6629 | 0.95025 | 0.94585 | 0.94139 | 0.95746 | 1370.02 | 1340.57 | 1316.12 | 1293.17 |
| 0.7536 | 0.96030 | 0.95598 | 0.95157 | 0.96271 | 1412.28 | 1383.10 | 1359.28 | 1338.56 |
| 0.8398 | 0.97027 | 0.96603 | 0.96170 | 0.96787 | 1460.23 | 1432.38 | 1409.42 | 1390.55 |
| 0.9219 | 0.98022 | 0.97604 | 0.97175 | 0.97286 | 1514.76 | 1489.98 | 1468.47 | 1450.86 |
| 1.0000 | 0.99019 | 0.98599 | 0.98169 | 0.97759 | 1578.50 | 1558.20 | 1538.50 | 1520.50 |

Standard uncertainties u are u (T) = 0.01 K, u ($\rho$) = ±0.0005 g cm$^{-3}$, u ($u$) = ± 0.5 m s$^{-1}$

Where $\kappa_s^{id}$is the ideal value of the isentropic compressibility and calculated by using Benson and Kiyohara [15–17] expression was given below:

$$\kappa_s^{id} = \phi_1 \kappa_{s,1} + \phi_2 \kappa_{s,2} + T\left[\frac{\phi_1 V_{m,1}(\alpha_{p,1})^2}{C_{p,1}} + \frac{\phi_2 V_{m,2}(\alpha_{p,2})^2}{C_{p,2}} - \frac{V_m^{id}\left(\alpha_p^{id}\right)^2}{C_p^{id}}\right] \tag{4}$$

where, $C_{pi}$and $\alpha_i$ are the molar heat capacity and the thermal expansion coefficient of the $i^{th}$ component respectively. The value of $C_{pi}$was obtained by group contribution method [18].

The thermal expansion coefficient $\alpha_i$ was calculated by following equation (5) [19].

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{5}$$

The excess $V_m^E$ and$\kappa_s^E$ values for the entire component were correlated with Redlich-Kister [20] polynomial equation,

$$Y^E = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i \tag{6}$$

Where $x_1$ and $x_2$ are the mole fractions of 2-methylaniline and alkyl acrylate. The standard deviation ($\sigma$) excess properties was calculated by using following equation,

$$\sigma = \left[ \frac{\sum (Y^E_{\mathrm{exp}} - Y^E_{cal})^2}{N - n} \right]^{\frac{1}{2}} \tag{7}$$

Where $N$ and n are the number of experimental points and number of coefficients. The values of adjustable parameters and standard deviations are presented in Table 4. The standard deviations values are found to be the highest level of confidence which gives the satisfactory results.

The calculated excess molar volume ($V_m^E$) with mole fraction ($x_1$) are presented in Table 3 and are depicted in Figures 1–3. The excess molar volume curves are almost symmetric and are parabolic in nature indicating negative deviations over the entire range of mole fraction. The

**Table 3.** Excess molar volume ($V_m^E$) and excess isentropic compressibility ($k_s^E$) of binary liquid mixtures of 2-methylaniline with alkyl acrylates at temperatures $T$ = (303.15 to 318.15) K.

| | $V_m^E$/cm$^3$.mol$^{-1}$ | | | | $k_s^E$/TPa$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| $x_1$ | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| 2-methylaniline + methyl acrylate | | | | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0844 | −0.0438 | −0.0504 | −0.0579 | −0.0649 | −3.5433 | −3.9779 | −4.5009 | −5.1596 |
| 0.1717 | −0.0771 | −0.0851 | −0.0926 | −0.0987 | −6.0866 | −6.6095 | −7.0815 | −7.4924 |
| 0.2622 | −0.1013 | −0.1095 | −0.1170 | −0.1227 | −7.6044 | −7.9711 | −8.3616 | −8.7385 |
| 0.3560 | −0.1153 | −0.1225 | −0.1312 | −0.1373 | −8.4363 | −8.7929 | −9.1596 | −9.5297 |
| 0.4533 | −0.1227 | −0.1303 | −0.1368 | −0.1440 | −8.7929 | −9.1596 | −9.5195 | −9.8863 |
| 0.5543 | −0.1173 | −0.1252 | −0.1320 | −0.1396 | −8.3107 | −8.6638 | −9.0747 | −9.4584 |
| 0.6593 | −0.1004 | −0.1095 | −0.1176 | −0.1255 | −7.2071 | −7.5874 | −8.0357 | −8.4907 |
| 0.7683 | −0.0752 | −0.0848 | −0.0922 | −0.1010 | −5.4550 | −5.8998 | −6.4160 | −6.8778 |
| 0.8818 | −0.0425 | −0.0520 | −0.0591 | −0.0665 | −3.0204 | −3.4007 | −3.8693 | −4.3922 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 2-methylaniline + ethyl acrylate | | | | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0998 | −0.0318 | −0.0429 | −0.0501 | −0.0593 | −3.1087 | −3.4542 | −4.0175 | −4.7210 |
| 0.1997 | −0.0626 | −0.0735 | −0.0826 | −0.0925 | −5.5645 | −6.0034 | −6.5979 | −7.0150 |
| 0.2996 | −0.0912 | −0.1022 | −0.1116 | −0.1194 | −7.0057 | −7.4103 | −7.9644 | −8.3814 |
| 0.3995 | −0.1076 | −0.1164 | −0.1238 | −0.1316 | −7.9644 | −8.3192 | −8.7269 | −9.1752 |
| 0.4995 | −0.1159 | −0.1247 | −0.1320 | −0.1389 | −8.3254 | −8.6491 | −9.0538 | −9.4989 |
| 0.5995 | −0.1080 | −0.1178 | −0.1260 | −0.1341 | −8.0017 | −8.3130 | −8.7643 | −9.1098 |
| 0.6996 | −0.0926 | −0.1040 | −0.1126 | −0.1209 | −6.8936 | −7.2391 | −7.7278 | −8.1822 |
| 0.7997 | −0.0709 | −0.0796 | −0.0889 | −0.0989 | −5.0603 | −5.5116 | −6.0252 | −6.5263 |
| 0.8998 | −0.0390 | −0.0462 | −0.0552 | −0.0633 | −2.7102 | −3.0993 | −3.5662 | −4.1234 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 2-methylaniline + butyl acrylate | | | | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1271 | −0.0271 | −0.0354 | −0.0438 | −0.0511 | −2.8812 | −3.3158 | −3.7504 | −4.2326 |
| 0.2468 | −0.0540 | −0.0649 | −0.0743 | −0.0812 | −5.1596 | −5.6384 | −6.0662 | −6.5212 |
| 0.3597 | −0.0776 | −0.0880 | −0.0957 | −0.1042 | −6.7216 | −7.1766 | −7.6112 | −7.9881 |
| 0.4663 | −0.0921 | −0.1011 | −0.1093 | −0.1162 | −7.5976 | −7.9983 | −8.4092 | −8.7793 |
| 0.5672 | −0.0983 | −0.1059 | −0.1133 | −0.1208 | −7.8659 | −8.2767 | −8.6808 | −9.0475 |
| 0.6629 | −0.0980 | −0.1054 | −0.1129 | −0.1195 | −7.2954 | −7.7368 | −8.1036 | −8.4873 |
| 0.7536 | −0.0847 | −0.0940 | −0.1021 | −0.1077 | −5.9270 | −6.4397 | −6.9762 | −7.3871 |
| 0.8398 | −0.0599 | −0.0703 | −0.0802 | −0.0889 | −4.2190 | −4.7114 | −5.2241 | −5.6893 |
| 0.9219 | −0.0291 | −0.0382 | −0.0468 | −0.0564 | −2.0051 | −2.5178 | −2.9423 | −3.4211 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Standard uncertainties u are u (T) = 0.01 K, u ($V_m^E$) = ± 0.005 cm$^3$. mol$^{-1}$, u ($k_s^E$) = 0.05 TPa$^{-1}$

**Table 4.** Coefficients of Redlich-Kister equation and corresponding standard deviations ($\sigma$) for 2-methylaniline + alkyl acrylates at temperatures $T$ = (303.15 to 318.15) K.

| Binary mixtures | Functions | $A_0$ | $A_1$ | $A_2$ | $\sigma$ |
|---|---|---|---|---|---|
| **T = 303.15 K** | | | | | |
| 2-methylaniline+ methyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.40039 | −0.04986 | 0.127078 | 0.000998 |
| | $\kappa_s^E/TPa^{-1}$ | −32.9056 | −8.0417 | −0.00207 | 0.089257 |
| 2-methylaniline+ ethyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.4564 | 0.029584 | 0.106564 | 0.001664 |
| | $\kappa_s^E/TPa^{-1}$ | −34.9161 | −2.96482 | −2.67738 | 0.0644 |
| 2-methylaniline+ butyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.47741 | 0.126449 | −0.00635 | 0.000975 |
| | $\kappa_s^E/TPa^{-1}$ | −0.47741 | 0.126449 | −0.00635 | 0.000975 |
| **T = 308.15 K** | | | | | |
| 2-methylaniline+ methyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.43009 | −0.0522 | 0.021872 | 0.00106 |
| | $\kappa_s^E/TPa^{-1}$ | −34.0946 | −8.04412 | −4.42242 | 0.091927 |
| 2-methylaniline+ ethyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.49191 | 0.020936 | 0.015794 | 0.001334 |
| | $\kappa_s^E/TPa^{-1}$ | −36.1819 | −3.18385 | −7.41414 | 0.090802 |
| 2-methylaniline+ butyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.47741 | 0.126449 | −0.00635 | 0.000975 |
| | $\kappa_s^E/TPa^{-1}$ | −0.50478 | 0.136233 | −0.09149 | 0.001335 |
| **T = 313.15 K** | | | | | |
| 2-methylaniline+ methyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.45749 | −0.05005 | −0.07185 | 0.001034 |
| | $\kappa_s^E/TPa^{-1}$ | −35.6232 | −8.33981 | −10.3334 | 0.136641 |
| 2-methylaniline+ ethyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.52062 | 0.023461 | −0.07226 | 0.001704 |
| | $\kappa_s^E/TPa^{-1}$ | −37.4873 | −3.02918 | −12.9918 | 0.12026 |
| 2-methylaniline+ butyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.53216 | 0.135716 | −0.15932 | 0.001874 |
| | $\kappa_s^E/TPa^{-1}$ | −0.53216 | 0.135716 | −0.15932 | 0.001874 |
| **T = 318.15 K** | | | | | |
| 2-methylaniline+ methyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.48138 | −0.04735 | −0.15965 | 0.001143 |
| | $\kappa_s^E/TPa^{-1}$ | −36.9716 | −8.2863 | −16.5527 | 0.21096 |
| 2-methylaniline+ ethyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.54744 | 0.023193 | −0.17163 | 0.001779 |
| | $\kappa_s^E/TPa^{-1}$ | −38.6956 | −2.97877 | −19.1064 | 0.195604 |
| 2-methylaniline+ butyl acrylate | $V_m^E/cm^3.mol^{-1}$ | −0.5553 | 0.146985 | −0.23552 | 0.002523 |
| | $\kappa_s^E/TPa^{-1}$ | −0.5553 | 0.146985 | −0.23552 | 0.002523 |

observed $V_m^E$ values are the resultant of physical and chemical forces and they are broadly recognised as:

1. The breaking of liquid order on mixing with second compound.
2. Non-specific physical interactions and unfavourable interactions between the unlike molecules.
3. Specific interactions appearing in the mixtures between the dissimilar molecules by dipole-dipole and by donor-acceptor complexes.

Generally, the first two factors contribute for the expansion of volume and the later factors contribute to diminish the volume. From the $V_m^E$curves shown in Figures 1–3. It is clear that in the case of 2- methylaniline with alkyl acrylate the volume reduction factors are preponderant. A careful analysis of data shown in Figures 1–3 reveals a contraction in the volume which is dominant in the binary liquid mixtures containing 2-methylaniline with alkyl acrylate. The mixing of 2-methylaniline with alkyl acrylate would induce mutual dissociation of dipolar interactions present in pure liquids and formation of new hydrogen bonds between $-NH_2$ group of 2-methylaniline and $-C=O$ group of alkyl acrylate leading to a contraction in the volume, which is the reason for negative $V_m^E$ values.

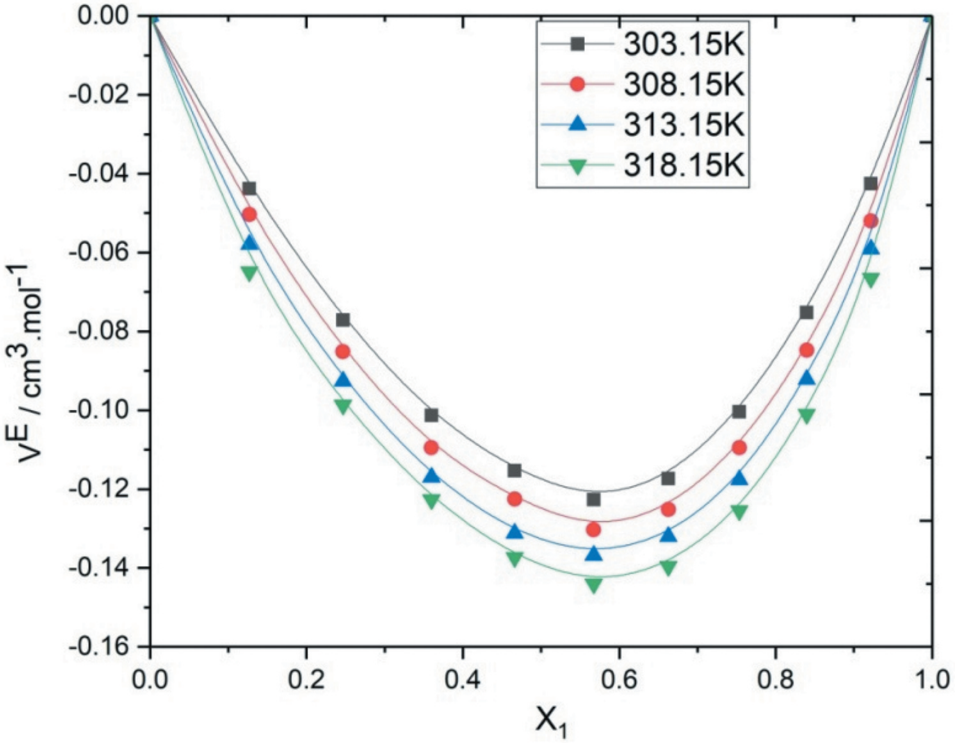

**Figure 1.** Variation of excess molar volume ($V_m^E$) with mole fraction ($x_1$) of 2-methylaniline +methyl acrylate at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (▼).

From Table 3, it can be observed that the $V_m^E$is more negative in the following order: **MA** < **EA** < **BA**, which suggests that there is an expansion in volume as we increase the alkyl chain length and the order of interaction: **MA** > **EA** > **BA**, this due to fact that as the size of alkyl group in acrylates molecules increases closer approach of 2-methylaniline and acrylate molecules becomes increasingly difficult due to steric hindrance, which results in decreased in interaction between unlike molecules, leading to expansion in volume. The increase in temperature results more monomers of alkyl acrylate, which better fit in to the structures of 2-methylaniline i.e. more packing effect by which the excess molar volume values are found more negative with increase in temperature.

The variation of excess isentropic compressibility ($\kappa_s^E$) at T = (303.15–318.15) K as a function of alkyl acrylate concentrations for mixtures are presented Table 3 and shown in Figures 4–6.An examination of Figures 4–6 shows that the $\kappa_s^E$ values are negative over the whole concentration range. The negative $\kappa_s^E$ be a sign of hydrogen bond formation between 2-methylaniline and alkyl acrylate that leads to closer packing of 2 MA and alkyl acrylate molecules resulting in a reduction in volume of the mixture [21]. The negative $\kappa_s^E$suggests that strong hydrogen bond between proton-donor and proton-acceptor groups in their molecules. Mixing of 2-methylaniline with alkyl acrylate would induce mutual dissociation of the hydrogen-bonded structures present in pure liquids with subsequent formation of new Hydrogen bonds (-C = O … .N and N-H … .O-C) between proton-acceptor nitrogen atom of – $NH_2$ group of 2-methylaniline and hydrogen atom of -C = O group(s) of alkyl acrylate molecules. Equally important is the formation of Hydrogen bond between hydrogen atoms of – $NH_2$ group of 2-methylaniline and oxygen atoms of – C = O groups of alkyl acrylate, leading to contraction in volume, which should result in negative $\kappa_s^E$values. The magnitude of $\kappa_s^E$follows the sequence: **MA** < **EA** < **BA**. The expansion in

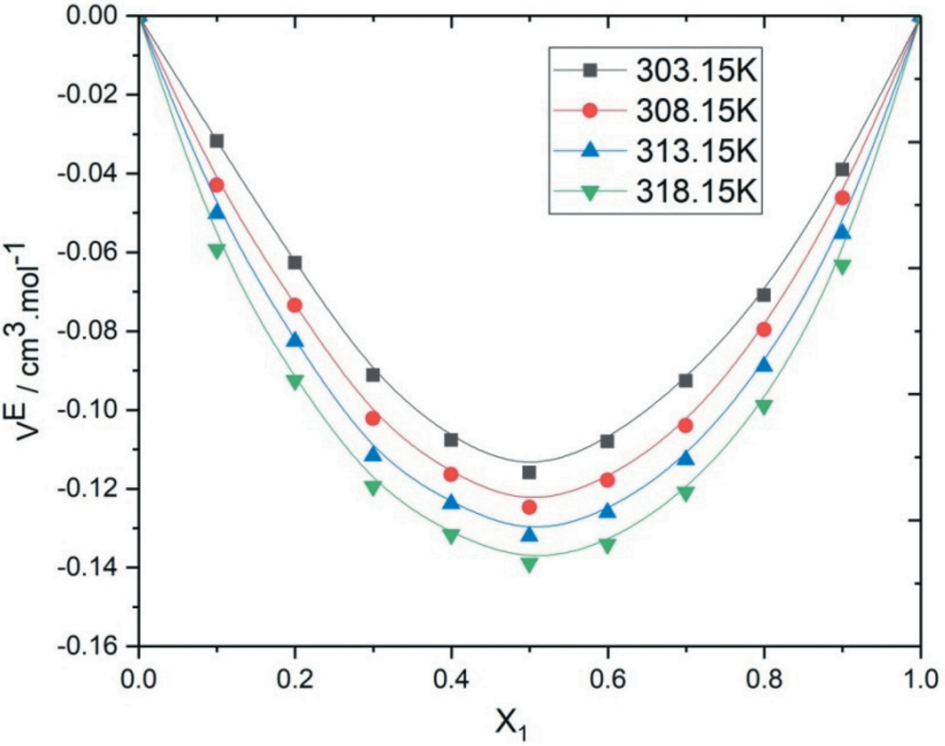

**Figure 2.** Variation of excess molar volume ($V_m^E$) with mole fraction ($x_1$) of 2-methylaniline +ethyl acrylate at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (▼).

volume from MA to n-BA increases the compressibility in the same order. When temperature increases $\kappa_s^E$ becomes more and more negative in the present system [22] . Increase in temperature promotes the breaking of associates present in the pure liquids releasing more and more free dipoles of unlike molecules in the mixture which interact with each other. As a result, excess values become more negative with rise in temperature. Studies show that $\kappa_s^E$ become increasingly negative as the strength of interaction between component molecules increases [23].

## 4.2. Geometrical optimisation

The geometrical optimised structures of 2-methylaniline and alkyl acrylate complexes have been computed by using B3LYP/6-311 G ++ (d, p) level of theory and are presented in Figures 7–12. Harmonic vibrational frequencies and Zero Point Energy Corrections (ZPE) were calculated for the optimised complexes and for the non-bonded molecules. None of the fully optimised complexes has imaginary frequencies. The hydrogen bond geometrical parameters of the two obtained associations (N-H … O = C-, N-H … O-C-) are presented in Table 5. During the formation of X-H … Y hydrogen bond, transfer of electrons were observed between X-H groups and Y group leading to the shortening of H … Y bond length. The shorter H … Y bond or the longer X-H bond is, the stronger interaction is attributed, and vice versa [3]. An examination of data in Table 5 indicates all the values of ΔR(X-H) are positive; these values indicate that they are all red shifting hydrogen bonds.

An examination of data in Table 5 indicates that the shortest hydrogen bond length (H … Y) ($1.92791A^0$) and largest $\Delta R(X-H)$values are found in COM 2 ($0.01276A^0$). This indicates N-H …. O = C hydrogen bond in **COM 29** (2-methylaniline – methyl acrylate) is the strongest hydrogen bond among all 2-methylaniline – alkyl acrylate complexes. The hydrogen bond in **COM 4** involving

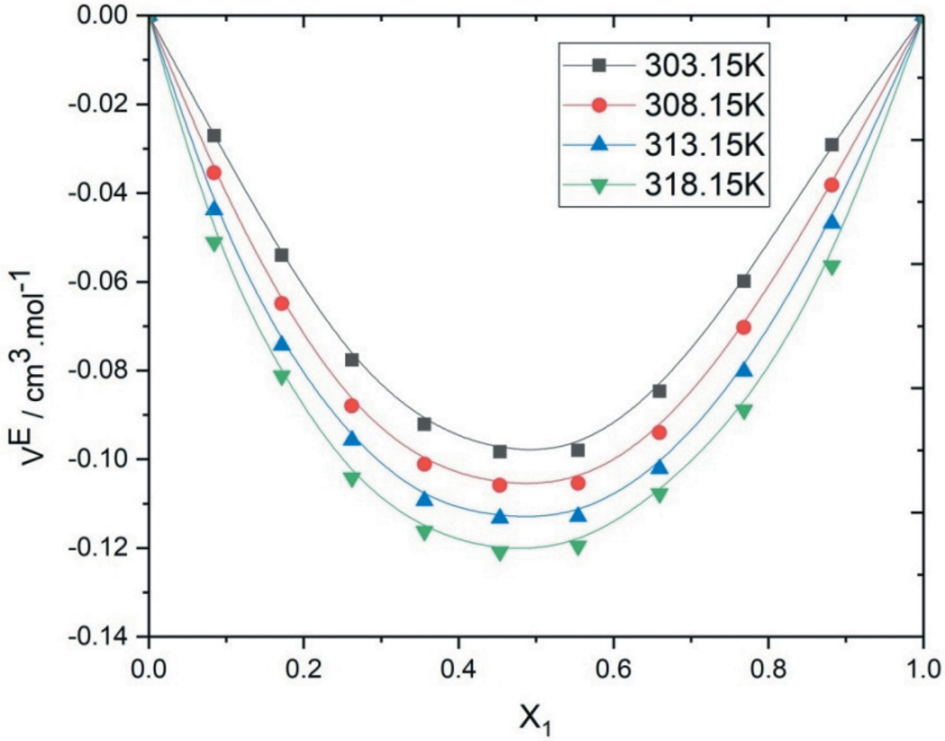

**Figure 3.** Variation of excess molar volume ($V_m^E$) with mole fraction ($x_1$) of 2-methylaniline +butyl acrylate at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (▼).

the second shortest hydrogen bond length ($1.93492A^0$) and the second largest value ($0.01245A^0$) of $\Delta R(X - H)$should be the second strongest hydrogen bond present in 2-methylaniline and ethyl acrylate complex. Similarly the N-H … O hydrogen bond present in **COM 6** is the third strongest hydrogen bond with a hydrogen bond length ($1.95515A^0$) and largest value $0.01183A^0$) of $\Delta R(X - H)$present in butyl acrylate. This is in good agreement with the experimental result.

## *4.3 Interaction energy*

The stability of the selected hydrogen-bonded complexes has been analysed by study of their interaction energies. The counterpoise-corrected interaction energies, $\Delta E^{cp}$for all the dimers were computed at DFT, B3LYP. All the corrected interaction energies are summarised in Table 6.

Among the 6 cross-associated hydrogen-bonded complexes the highest interaction energy is observed in 2-methylaniline- methyl acrylate complex (**COM 2**) with N-H … O hydrogen bond of interaction energy −12.440 KJ.mol$^{-1}$. The second highest interaction energy is observed in 2-methylaniline – ethyl acrylate complexes **COM 4** with hydrogen bond of interaction energy −10.312 KJ.mol$^{-1}$. The third highest interaction energy is observed in cross-association of 2-methylaniline-butyl acrylate complexes **COM 6** with hydrogen bonds of interaction energy −9.1818 KJ.mol$^{-1}$, Which coincides with the result of the geometrical optimisation.

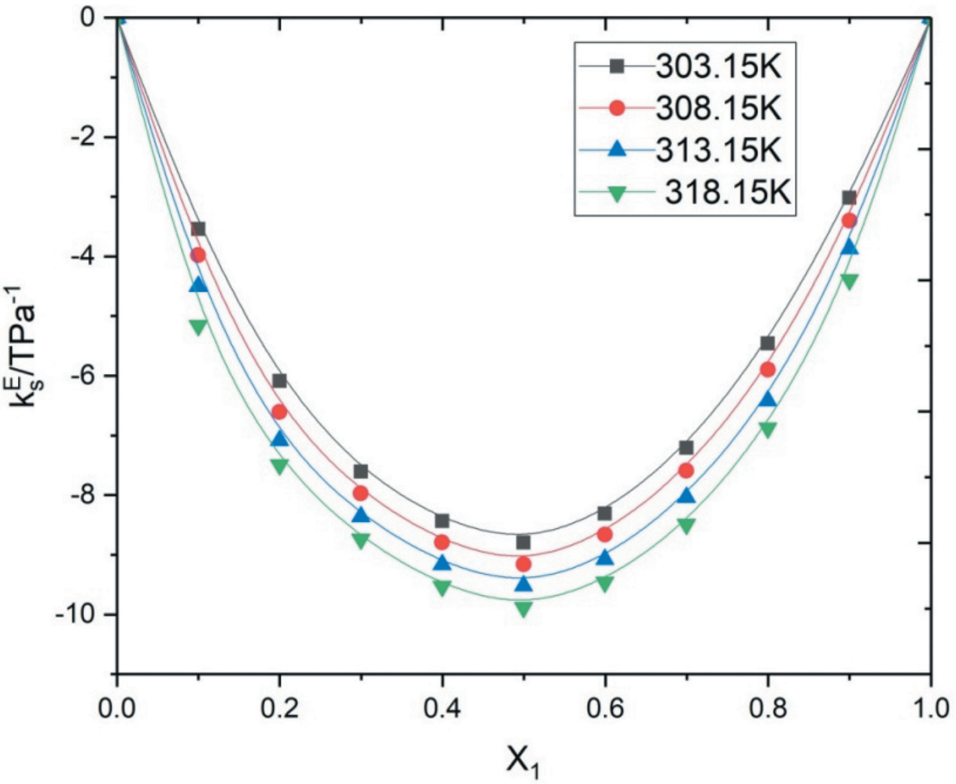

**Figure 4.** Variation of excess isentropic compressibility ($\kappa_S^E$) with mole fraction ($x_1$) of 2-methylaniline + methyl acrylate at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (▼).

### 4.4. Quantum theory of atoms in molecules (QTAIM) analysis

The QTAIM theory of $\rho(r)$and $^{2}\rho(r)$ for the hydrogen bonds [24] would be an excellent method to study the strength of the closed shell interactions formed between the given complexes. The values of QTAIM topological parameters of the electron density ($\rho(r)$) and Laplacian of the electron density ( $^{2}\rho(r)$ at BCP of N-H … O = C-, N-H … O-C intermolecular hydrogen bond for all dimers are shown in Table 7. The values of the$\rho(r)$, $^{2}\rho(r)$ in Table 7 are positive which indicate that electronic charge is depleted along the bond length indicates closed-shell interactions like intermolecular hydrogen interactions. Shortest hydrogen bond corresponds the largest value of value of$\rho(r)$.

As shown in the Figure 8, Figure 10 and Figure 12 the complexes **COM 2, COM 4** and **COM 6** shows N-H … O = C- hydrogen bonds have high electron density values (0.02952, 0.02694and 0.02478) and positive Laplacian electron density ( $^{2}\rho(r)$) values (0.10315, 0.08403 and 0.09403). These values shows that N-H … O = C interactions are closed-shell interactions. Where as in the complexes **COM 1, COM 3** and **COM 5** shows N-H … O-C hydrogen bonds have $\rho(r)$ values (0.02341, 0.02081and 0.0197) and positive Laplacian electron density ( $^{2}\rho(r)$) values (0.08412, 0.07317 and 0.06981). These values also indicate that N-H … O-C interactions are also closed shell interactions [25]. From topological analysis it is observed that N-H … O = C interactions are more strong N-H … O-C interactions.

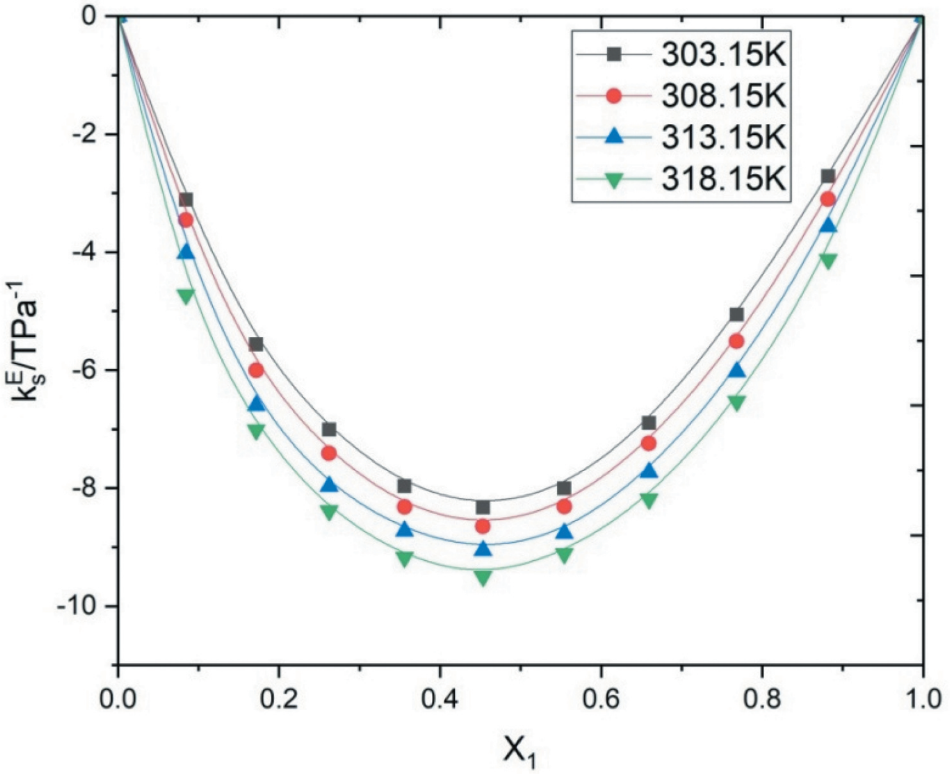

**Figure 5.** Variation of excess isentropic compressibility ($\kappa_s^E$) with mole fraction ($x_1$) of 2-methylaniline + ethyl acrylate at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (▼).

## 4.5. NBO analysis

To get more detailed information on hydrogen bond interactions, NBO analysis has been performed. NBO analysis is used to engender information on the changes of charge densities in proton donor and proton acceptor as well as the changes in the bonding and antibonding space. Since, the hydrogen bonds are formed due to the charge density transfer from the proton acceptor to proton donor; the amount of charge transfer to the proton donor and the other bonds is a crucial point for the elongation and contraction of X–H bond. Hence the donor–acceptor (bond–antibond) interactions are taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbital's and then estimated their energies by second order perturbation theory. The second-order perturbation stabilisation energy for proton donor–acceptor interaction relevant to hydrogen bond formation in 2-methylaniline and isomeric butanediol complex from NBO analysis at B3LYP/6311 G++ (d,p) level of theory and are presented in Table 8.

The orbital interactions LP (O)→σ(N-H)*, in 2-methylaniline and methyl acrylate complexes (**COM 1 – COM 2**) have second-order perturbation stabilisation energies(E(2)) are 13.423 and 19.643 kcal·mol$^{-1}$, while the orbital interactions LP(O)→σ (N-H)* in 2-methylaniline and ethyl acrylates complexes **COM 3 – COM 4** having stabilisation energies (E (2)) in the range of 13.130 and 16.790 kcal·mol$^{-1}$.The orbital interactions LP (O) →σ(N-H)*, LP(N) →σ(O-H)* in 2-methylaniline and butyl acrylate complexes **COM5 – COM 6** have second-order perturbation stabilisation energies E(2) have 5.880 and 13.784 kcal·mol$^{-1}$. Hence, it is observed that large amount of charge is transferred from lone pair of hydrogen atom of 2-methylaniline to the anti-bonding orbital of O = C

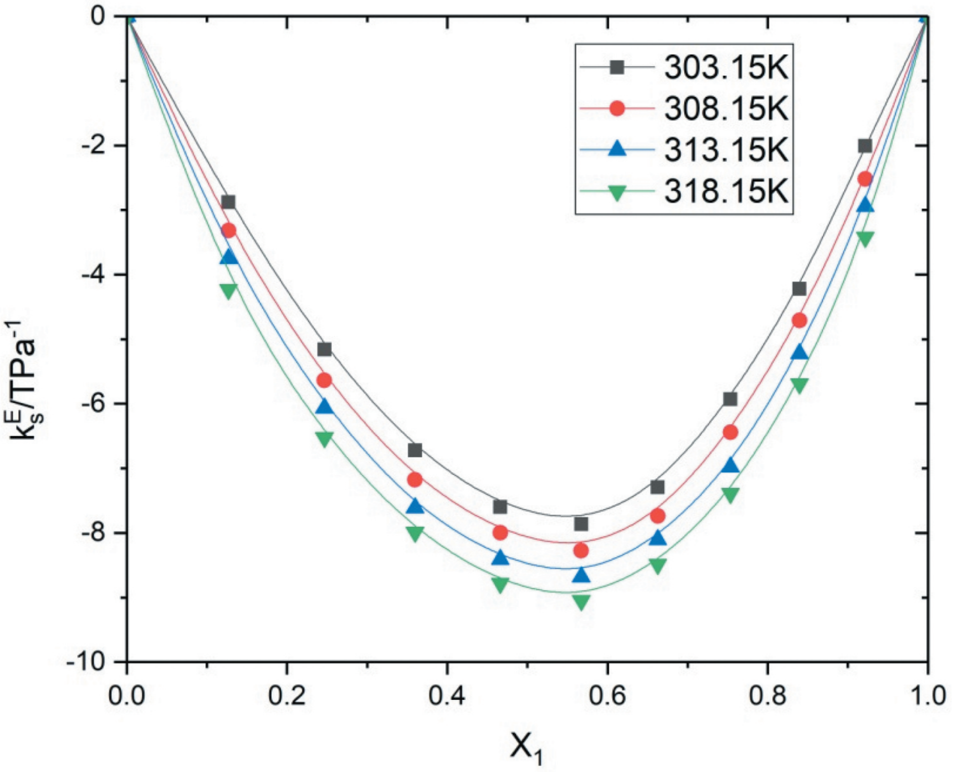

**Figure 6.** Variation of excess isentropic compressibility ($\kappa_s^E$) with mole fraction ($x_1$) of 2-methylaniline +butyl acrylate at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (▼).

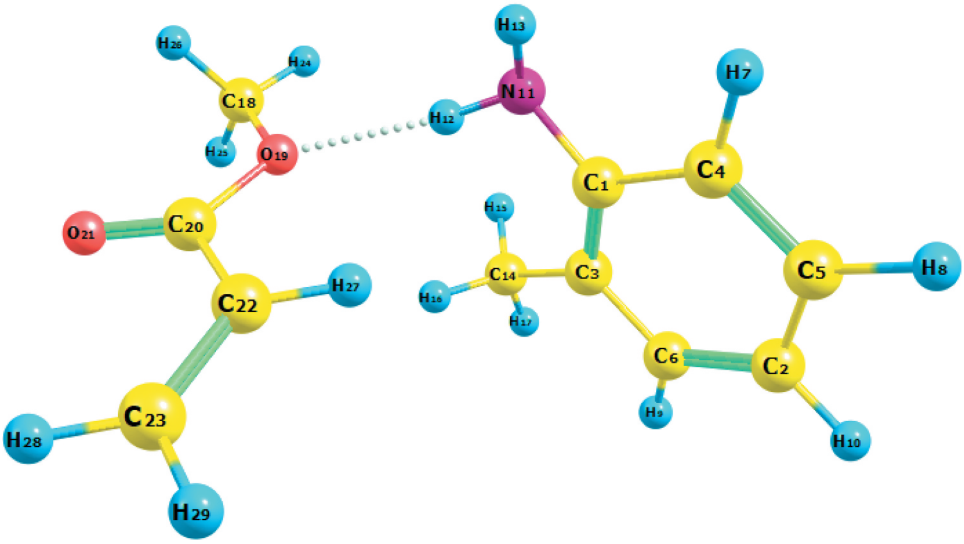

**Figure 7.** Optimised structure of 2 MA-MA (COM1).

**Table 5.** Distances (A$^0$) and angles ($^0$) of the hydrogen bonds for all hydrogen bond associations at B3LYP/6-311++G (d, p).

| Complexes | X-H . . . .Y | R(X-H) | ΔR (X-H) | R(H . . . .Y) | ΔR(H . . . Y) | R(X . . . Y) | (XHY) |
|---|---|---|---|---|---|---|---|
| COM 1 | N11-H12 . . . O19 | 1.01814 | 0.00872 | 2.08121 | 0.65874 | 3.09359 | 169.9 |
| COM 2 | N11-H12 . . . O21 | 0.96585 | 0.01276 | 1.92791 | 0.81204 | 2.89672 | 176.2 |
| COM 3 | N11-H13 . . . O22 | 1.01845 | 0.00903 | 2.08277 | 0.65719 | 3.09748 | 165.7 |
| COM 4 | N11-H13 . . . O21 | 0.96616 | 0.01245 | 1.93492 | 0.80581 | 2.90139 | 179.3 |
| COM 5 | N11-H12 . . . O22 | 1.01845 | 0.00903 | 2.08977 | 0.65096 | 3.10215 | 163.03 |
| COM 6 | N11-H12 . . . O26 | 0.9674 | 0.01183 | 1.95515 | 0.78558 | 2.91306 | 176.01 |

**Table 6.** Interaction energy corrected with BSSE ($\Delta E_{cp}$. kJ. mol$^{-1}$) for all dimmers at B3LYP/6-311++G (d, p) level.

| Complexes | X-H . . . .Y | $\Delta E$ | BSSE | $\Delta E_{cp}$ |
|---|---|---|---|---|
| COM1 | N11-H12 . . . O19 | −10.60781 | 1.71 | −8.89781 |
| COM 2 | N11-H12 . . . O21 | −13.54075 | 1.10 | −12.4408 |
| COM 3 | N11-H13 . . . O22 | −10.78183 | 1.60 | −9.11156 |
| COM 4 | N11-H13 . . . O21 | −11.72199 | 1.41 | −10.312 |
| COM 5 | N11-H12 . . . O22 | −7.71307 | 1.12 | −6.59307 |
| COM 6 | N11-H12 . . . O26 | −11.47156 | 2.36 | −9.18183 |

**Table 7.** Topological Properties (in a.u.) of the BCPs of intermolecular H-bonds in 2-methylaniline and **alkyl acrylates** complexes obtained from the B3LYP/6-311++G (d, p) level calculations.

| Complexes | X-H . . . .Y | $\rho$ | $^2\rho$ |
|---|---|---|---|
| COM1 | N11-H12 . . . O19 | 0.02341 | 0.08412 |
| COM 2 | N11-H12 . . . O21 | 0.02952 | 0.10315 |
| COM 3 | N11-H13 . . . O22 | 0.02081 | 0.07317 |
| COM 4 | N11-H13 . . . O21 | 0.02694 | 0.08403 |
| COM 5 | N11-H12 . . . O22 | 0.0197 | 0.06981 |
| COM 6 | N11-H12 . . . O26 | 0.02478 | 0.09403 |

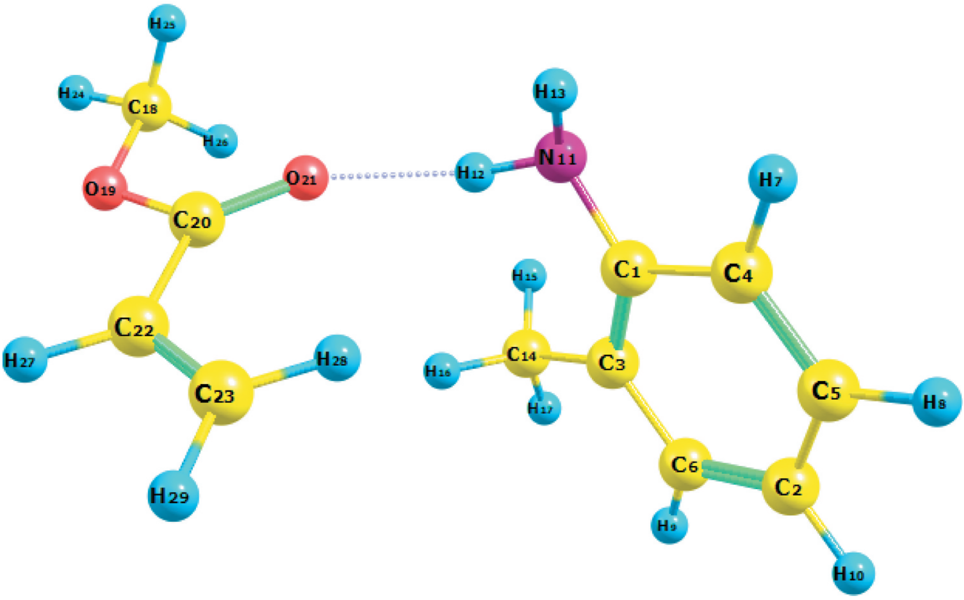

**Figure 8.** Optimised structure of 2 MA-MA (COM2).

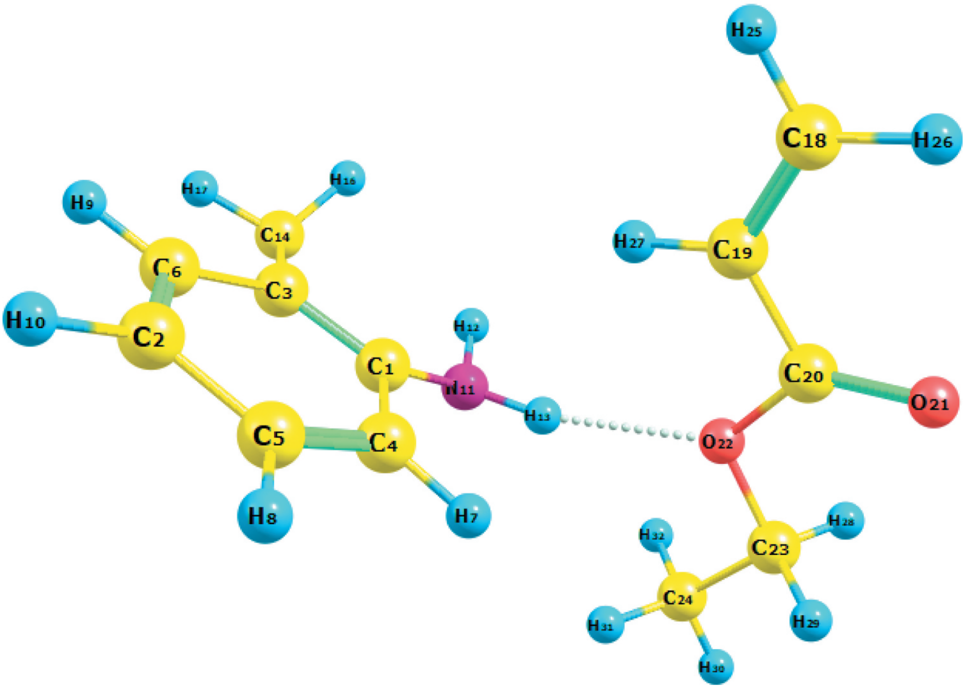

**Figure 9.** Optimised structure of 2 MA-EA (COM3).

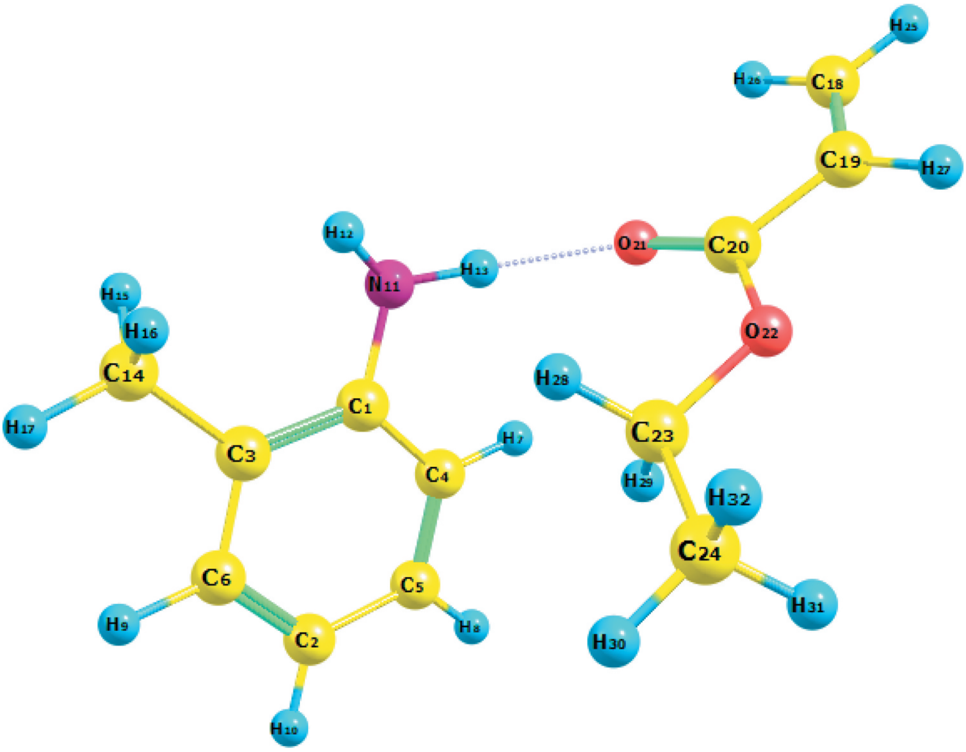

**Figure 10.** Optimised structure of 2 MA-EA (COM4).

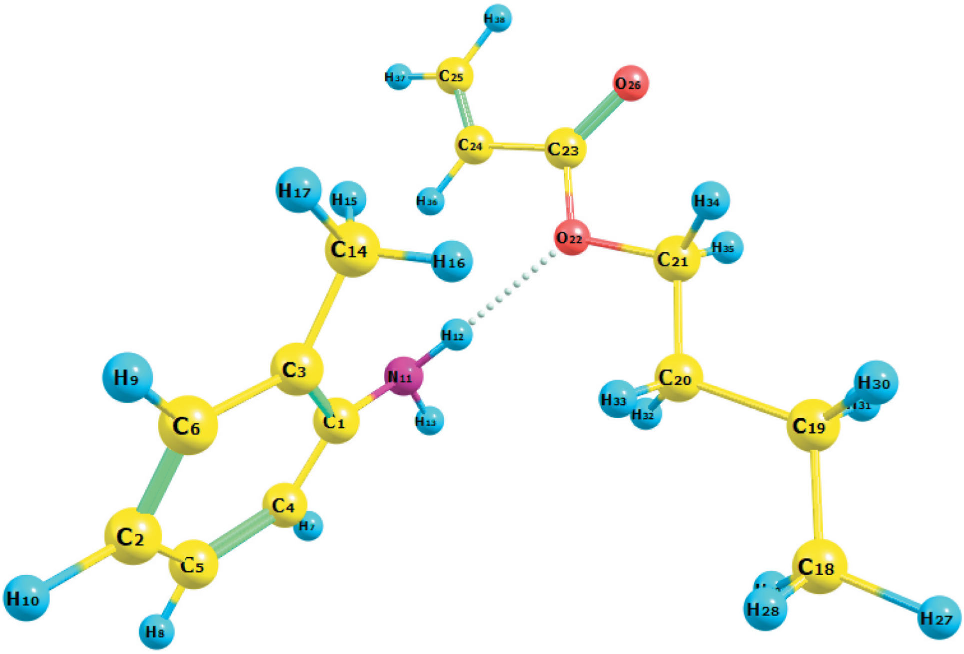

Figure 11. Optimised structure of 2 MA-BA (COM5).

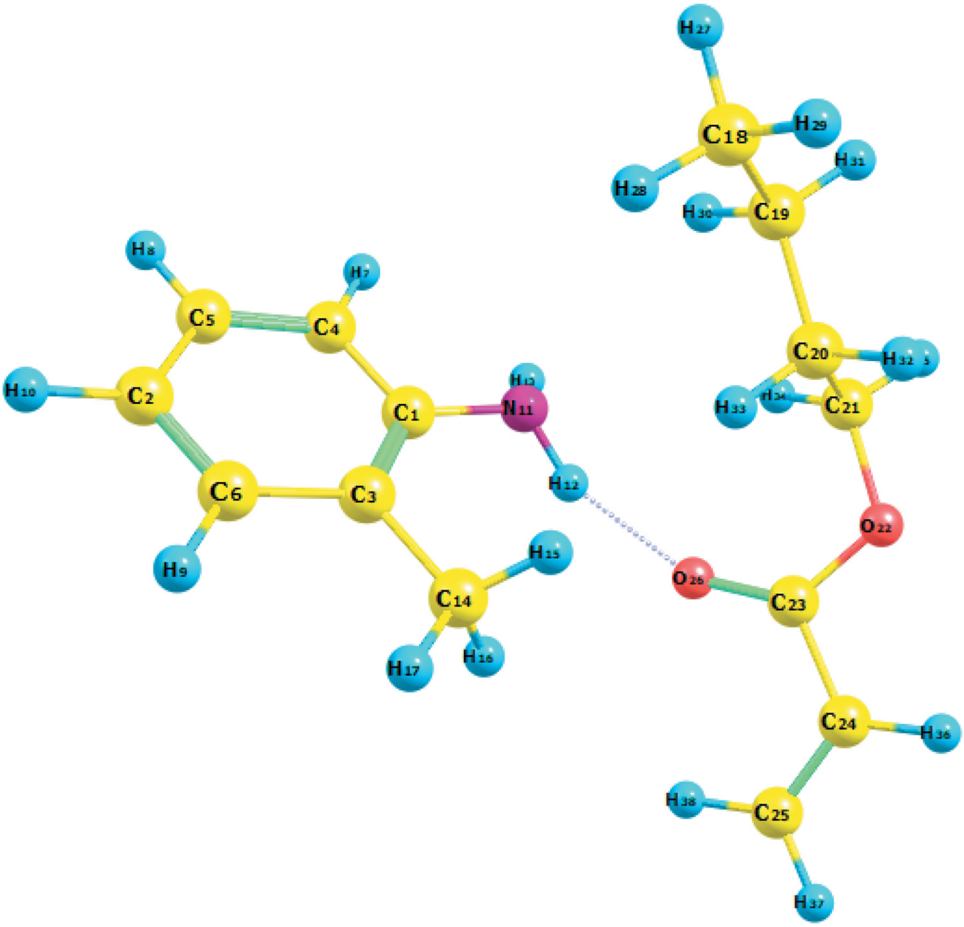

Figure 12. Optimised structure of 2 MA-BA (COM6).

**Table 8.** Second-perturbation energies (E(2)/kJ·mol$^{-1}$) of hydrogen bonds for all hydrogen bond associations obtained by NBO analysis at the B3LYP/6-311++G (d, p) level.

| Complexes | Donor NBO(i) | Acceptor NBO(j) | E(2) |
|---|---|---|---|
| COM 1 | LP(1) O19 | BD*(1)N11-H12 | 13.4236 |
| COM 2 | LP(1) O21 | BD*(1)N11-H12 | 19.6434 |
| COM 3 | LP(1) O22 | BD*(1)N11-H13 | 13.13016 |
| COM 4 | LP(1) O21 | BD*(1)N11-H13 | 16.79089 |
| COM 5 | LP(1) O22 | BD*(1)N11-H12 | 5.88087 |
| COM 6 | LP(1)O26 | BD*(1)N11-H12 | 13.78438 |

bond of butyl acrylate which reveals the most stable hydrogen bond complex compared to other alkyl acrylate complexes. This coincides with the compared result of the interaction energies calculation.

## 5. Conclusion

The volumetric, structural properties and intermolecular interactions in 2-methylaniline + alkyl acrylate are studied using a combined experimental and theoretical approach. Excess properties ($V_m^E$,$k_s^E$)derived from the experimental data of density and speed of sound at temperatures from 303.15 K to 318.15 K were observed to be negative at all mixtures. The negative-derived excess properties are due to volume contraction, interstitial accommodation of unlike molecules in mixtures. The intermolecular interaction observed to strong in case of 2-methylaniline and methyl acrylate mixture than 2-methylaniline and ethyl acrylate/butyl acrylate mixtures. The study of optimised geometries, interaction energies, QTAIM and NBO reveals that, **COM 2** (2-methylaniline- methyl acrylate) with N-H … O = C hydrogen bond is the most stable complex among the cross-associated dimers.

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## Disclosure statement

No potential conflict of interest was reported by the author.

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