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DFT study on thermodynamic properties of liquid mixtures containing cyclohexanol with aniline and chloro-substituted anilines

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ABSTRACT

Density (ρ) and speed of sound (u) findings on the binary liquid mixtures consisting of cyclohexanol (CH—OH), with aniline (A), *ortho*-chloroaniline (*o*-CA), and *meta*-chloroaniline (*m*-CA) were gathered at the various temperatures spanning the entire concentration range. 303.15, 308.15,313.15 and 318.15 K at atmospheric pressure. The information measured there was utilized to compute excess molar volume (V_m^E), excess isentropic compressibility (K_S^E), excess of speed of sound (u^E), excess intermolecular free length (L_f^E) and excess acoustic impedance (Z^E). Further, the partial molar volumes ($\overline{V}^\circ_{m,1}$. $\overline{V}^\circ_{\phi,1}$. $\overline{V}^\circ_{m,2}$. $\overline{V}^\circ_{\phi,2}$), partial molar compressibilities ($K^\circ_{m,1}$, $\overline{K}^\circ_{\phi,1}$, $\overline{K}^\circ_{m,2}$, $\overline{K}^\circ_{\phi,2}$) and their excess values ($\overline{V}^E_{m,1}$. $\overline{V}^{\circ E}_{\phi,1}$. $\overline{V}^E_{m,2}$. $\overline{V}^{\circ E}_{\phi,2}$), ($\overline{K}^E_{m,1}$, $\overline{K}^{\circ E}_{\phi,1}$, $\overline{K}^E_{m,2}$, $\overline{K}^{\circ E}_{\phi,2}$) were also computed to perceive more information on molecular interaction and structural effects in these mixtures. Applying the theory of Prigogine–Flory–Patterson (PFP) as a framework, the V_m^E data of the current liquid mixtures were examined. The analysis of the experimental data took into consideration the interactions that occur between the individual molecules that make up liquid mixtures. By using density functional theory DFT (B3LYP) of 6-31 ++ G (d,P) to analyze the geometries, bond characteristics, interaction energies, and hydrogen bonded complexes in organic solvent phase, quantum chemical calculations were able to further confirm the hydrogen bonding that predominates between cyclohexanol with aniline and chlorosubstituted anilines.

1. Introduction

Excess thermodynamic properties of binary liquid mixtures one of the essential tool for the process of developing industrial machinery and interpretation of solution theories. The deviation from ideal behaviour is observed when polar compounds are involved which are under the investigation. The volumetric and acoustic properties of binary mixtures are useful for the estimation of nature and strength of intermolecular interactions between component molecules [1,2]. Excess molar volume (V_m^E), excess isentropic compressibility (K_S^E), are useful to estimate strength of molecular interactions and to test solution theories and mathematical models [3] and for development of separation techniques and equipment, and for many potential industrial applications [4]. The liquid components that are under well-known organic liquids are the subject of this inquiry; in addition to being utilized as a raw material in industries and for ordinary analytical work, they were selected because they have a broad range of applications in numerous domains of chemistry. Cyclohexanol (an alcohol) can act as a hydrogen bond donor because of the hydroxyl (—OH) group. An essential intermediate substance, cyclohexanol is utilized extensively in the synthesis of hexanedioic acid and hexamethylenediamine, both are used as an important material for production of nylon, capro-lactum. Aniline and its chloro derivatives (*o*-chloroaniline, *m*-chloroaniline) have an amino (—NH_2) group, which can act as a hydrogen bond acceptor through the nitrogen atom.

Further, it is also used as a plasticizer, and stabilizer in the manufacture of paints, varnishes, and lacquers, *ortho* and *meta* chloroanilines are widely used in polymers, rubber,

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pharmaceutical, dye industries and in organic synthesis. Aniline finds its primary use in the production of rubber accelerators, antioxidant substances dyes and intermediary compounds, photographic chemicals, urethane foams, explosives, refined petroleum products, and fungicides and herbicides. The hydrogen bond strength chloro substituents (Cl) in different positions (*ortho*- and *meta*-) on the aniline ring could influence the strength of the hydrogen bonds. This happens because the electron-withdrawing nature of chlorine can alter the electron density on the nitrogen atom, impacting the ability of the amine group to participate in hydrogen bonding. This work provides fresh experimental information on the densities (ρ) and speed of sounds (u) measured at various temperatures 303.15, 308.15, 313.15, and 318.15 K for binary liquids mixtures of cyclohexanol + aniline and chloro substituted anilines across the composition range. Additionally, the partial molar characteristics were verified and the thermodynamic properties were examined using this experimental data. The results were computed, and the polynomial formulas were used to analyze the excess qualities. In addition, to verify their suitability, sound velocity data for fluid mixtures were analyzed at various temperatures under experimental conditions applied to Jacobson's free length theory (FLT) and Schaff's collision factor theory (CFT). To the best of our knowledge, the binary mixture of cyclohexanol + aniline and chloro substituted anilines has not had any experimental data for densities or speed of sound published in the literature. This is a portion of our continuing investigation on the thermodynamic characteristics of liquid mixes that comprise polar and protic solvents [5–9]. Here, we present unique outcomes from experiments for the above systems. Furthermore, we computed the electronic structure of molecular systems using the density functional theory (DFT), which is a highly accurate mathematical approach for replicating experimental data related to molecule geometry, frequency vibrational, atoms charges, adipole moment, and thermodynamic characteristics [10–13].

2. Experimental

All chemicals were purchased (A.R. grade) from Sigma Aldrich and SD. The mass percentage purity of all substances utilized in this investigation has been verified, and the method of purification and expected purity analysis technique are provided in Table 1. To make the binary liquid mixes, an electronic balance (A foset, ER 120A, India) was used to a suitable quantity of pure liquids should be weighed with a precision of ±0.1 mg. In order to minimize evaporation loss, the liquid substances were then syringed into sealed, airtight bottles. The estimation of the mole fraction has an error of $\pm 1 \times 10^{-4}$. With an error of $\pm 5 \times 10^{-3}$ kg·m^{-3}, with the aid of an Anton Paar DMA 5000 computerized swinging U-tube densimeter using, the density values (ρ) of the binary mixtures and matching chemical compounds were determined. Instrument of supplier of Mittal enterprises India Pvt. Ltd., New Delhi. M81, speed of sound of liquids that are pure and their liquid mixtures was measured using a single crystal ultrasonic instrument of variable route waves analysers running at a frequency of 2 MHz [14]. The estimated uncertainty in density and excess volume was found to be $\pm 5 \times 10^{-5}$ g·cm^{-3} and ±0.002 cm^3·mol^{-1} respectively. The details of the methods and methods of measuring were described earlier [15,16]. By evaluating the ρ and u of the experimental solutions with those described in Refs. [17–34], the purity of the solutions was carefully examined and the results were provided in Table 2. In addition, The Gaussian 03W programme was used to perform all of the quantum chemistry calculations using the DFT (B3LYP 6-31 ++G (d, p)) basis sets [35]. Both the visual animation and the validation of the normal mode assignment were investigated using the Gauss view software [36]. Utilizing density functional theories (DFT), the optimal molecule's energy absorption spectra were found.

Table 1
The specifications pure components.

Chemical	Source	CAS number	Purity in mass fraction	Linear formula
Cyclohexanol	Sigma Aldrich, India	108-93-0	≥0.98	$C_6H_{11}OH$
m-Chloro aniline	Sigma Aldrich, India	108-42-9	0.98	C_6H_6ClN
o-Chloro aniline	S.D fine Pvt. Ltd.	95-51-2	0.98	C_6H_6ClN
Aniline	Sigma Aldrich, India.	62-53-3	>0.99	$C_6H_5NH_2$

An extensive a review of the scientific literature demonstrates those binary combinations' more physicochemical characteristics of cyclohexanol with chlorotoluenes [37], *n*-alkanes [38] with alkylamines [23], alkanols [39,40], acetone [41]. They were recorded. As far as we are aware, excess thermodynamic characteristics: (V_m^E, K_S^E, L_f^E, Z^E and u^E) are not available in literature for the liquid mixtures of cyclohexanol with aniline, *ortho*-chloroaniline (*o*-CA) and *meta*-chloroaniline (*m*-CA). Hence, we have undertaken the present investigation of above said properties, for the mixtures of aniline molecules chloro compound and changing its location from *ortho* to *meta* position that may influence both the sign and magnitude of excess thermodynamic properties.

3. Results and Discussion

The measured density (ρ) and the speed of sound (u) of binary liquid mixtures of cyclohexanol with aniline and chloro substituted anilines, Throughout the entire composition range reported as mole fraction x_1 of cyclohexanol. ($0 \leq x_1 \leq 1$) are Table 3 lists the values, which are visually illustrated in Figs. S1 and S2, at 303.15, 308.15, 313.15, and 318.15 K, respectively. For all examined systems, ρ and u values drop with increasing temperature in the following order: cyclohexanol (CH—OH), aniline (A), *ortho*-chloroaniline (*o*-CA), and *meta*-chloroaniline (*m*-CA).

Eq. (1) was used to fit the experimental data of ρ and u to a polynomial formula [6].

$$F(x) = \sum_{i=1}^{k} A_i x_1^{i-1} \tag{1}$$

Table 4 provides a summary of the coefficient values A_i and standard deviations σ for both ρ and u data.

3.1. Excess molar volume (V_m^E)

To calculate the excess molar volumes data, apply for the following formula was utilized.

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

where ρ and ρ^* are the densities of the combination and the density of the pure liquid molar mass of element I in composed is represented by M_i, and its mole fraction is represented by x_i. Table S1 contains the observed excess molar volumes., and are graphically represented at all the four temperatures in Fig. 1. The measured systems (V_m^E, K_S^E, L_f^E, Z^E and u^E) values were matched with the Redlich–Kister [42] Eq. (3) in the following way:

Table 2
Experimental and literature values of density (ρ), speed of sound (u) and heat capacity (C_P) of pure liquids at different temperatures.

Liquids	T/K	ρ/kg·m^{-3}		u/m·s^{-1}		C_P/J·K^{-1}·mol^{-1}
		Expt.	Lit.	Expt.	Lit.	Expt.
Cyclohexanol	303.15	0.94141	0.94143 [23]	1444.2	1443.2 [24]	135.68 [35]
	308.15	0.93726	0.93723 [24]	1425.1	1419.6 [23]	137.83 [35]
	313.15	0.93341	0.93348 [24]	1415.3	1414.2 [23]	139.98 [35]
	318.15	0.92805	0.92811 [24]	1381.6	1380.8 [23]	142.10 [35]
m-Chloro aniline	303.15	1.20540	1.20532 [19]	1518.3	1517.5 [19]	204.64 [35]
			1.20530 [30]		1517.0 [26]	
	308.15	1.20068	1.20075 [19]	1501.4	1501.2 [19]	205.38 [35]
			1.20075 [30]			
	313.15	1.19603	1.19600 [19]	1480.7	1480.3 [19]	206.12 [35]
			1.19602 [30]			
	318.15	1.19132	1.19125 [19]	1465.2	1464.8 [19]	206.8 [35]
			1.19125 [30]			
o-Chloro aniline	303.15	1.20268	1.20269 [17]	1469.5	1469.6 [17]	171.54 [35]
			1.2026 [27]		1469.6 [25]	
			1.2027 [29]		1469.5 [27]	
					1470 [26]	
	308.15	1.19798	1.19802 [17]	1452.4	1452.8 [18]	173.14 [35]
			1.19802 [18]		1453.4 [27]	
			1.1980 [27]		1455.13 [28]	
			1190.62 [28]			
	313.15	1.19296	1.19302 [17]	1436.1	1435.9 [18]	173.54 [35]
			1.19302 [18]		1435.3 [27]	
			1.1930 [27]		1436 [26]	
	318.15	1.18843	1.18849 [17,18]	1419.2	1418.9 [17]	174.25 [35]
			1.1884 [27]		1418.9 [18]	
					1418.8 [27]	
Aniline	303.15	1.01320	1.01318 [20,21]	1614.8	1614.5 [22]	193.2 [35]
			1.0129 [31]		1615.0 [34]	
			1.0130 [32]			
			1.01317 [33]			
			1.0172 [34]			
	308.15	1.00887	1.00885 [22]	1606.4	1606.5 [22]	194.4 [35]
			1.0086 [31]		1606.6 [34]	
			1.00890 [33]			
			1.0085 [18]			
	313.15	1.00438	1.0042 [31]	1586.2	1586.0 [22]	195.6 [35]
			1.00463 [33]		1586.6 [34]	
			1.0048 [34]			
	318.15	1.00037	1.00036 [33]	1572.6	–	196.8 [35]

Note: The standard uncertainties are $u(\rho) = \pm 0.6 \times 10^{-4}$ g·cm^{-3}, $u(u) = \pm 0.7\%$, $u(T) = 0.01$ K for density, $u(T) = 0.02$ K for speed of sound and $u(p) = 1$ kPa.

$$F(x) = x_1 x_2 \sum_{i=1}^{k} a_i (x_1 - x_2)^{i-1} \quad (3)$$

where a_i is the determinants of polynomials equations, k is the measured by polynomial degree, and all the excess properties represents by $F(x)$. The values of coefficients a_i and stranded deviations σ for excess properties are given in Table 5.

An investigation of V_m^E curves in Fig. 1 for the systems of cyclohexanol with aniline, *ortho*-chloroaniline, and *meta*-chloroaniline indicate that the V_m^E data is more negative in the binary system containing aniline at all the investigated temperatures at 303.15 K. The maximum negative V_m^E data was seen at mole-fraction range for the systems cyclohexanol + aniline ($X_1 = 0.4995$, $V_m^E = -0.9819$, cyclohexanol + *o*-chloroaniline ($X_1 = 0.6010$, $V_m^E = -0.5244$, and cyclohexanol + *m*-chloroaniline ($X_1 = 0.5683$, $V_m^E = -0.4770$). The negative V_m^E reveal that on mixing of component molecules attractive interactions or more effective packing is observed between component molecules. It was well established that, large negative deviations arised from effective interactions between component molecules, and interstitial accommodation, are causing a perfect state in certain combinations. [5,43–46]. The interactions may hydrogen bonds and the combination of dipole interactions between incompatible compounds. An examination of V_m^E curves suggest that the binary mixture containing cyclohexanol + aniline is producing more negative (V_m^E) values when compared to the isomers of chloroaniline meolecules. This may be clearly explained by considering the following facts:

Aniline is more basic than (*o*-CA) and (*m*-CA). The basicity of aniline and its derivatives is impacted of the presence of substituents on the benzene ring. Aniline is a primary aromatic amine that can accept a proton to for anilinium ion ($C_6H_5NH_3^+$) and the lone pair of electrons on the nitrogen atom in aniline is available for protonation.

When chlorine atoms are attached to the benzene ring as *ortho*-chloroaniline or *meta*-chloroaniline, the inductive action of the chlorine changes the net electron density on the nitrogen atoms, since chlorine is an electron withdrawing group, which decreases the availability of the lone pair of electrons on the nitrogen atom for protonation. This reduces the basicity of chloroanilines when compared to aniline. Among *ortho*-chloroaniline and *meta*-chloroaniline mixtures, the intermolecular interactions are minimum in the mixture containing *meta*-chloroaniline.

Basicity refers to a property of a compound to accept protons (H^+). In the case of amino compounds, the basicity is influenced by electron donating or electron–withdrawing nature of substituents on the aromatic ring. The chloro group (–Cl) is an electron withdrawing group, due its electro negativity. This leads to reduction in

Table 3
Densities ρ and speeds of sound u for cyclohexanol with aniline and chloro substituted anilines systems at different temperatures.

x_1	$\rho \times 10^{-3}$/kg·m^{-3}				u/m·s^{-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
Cyclohexanol (1) + *m*-CA								
0.0000	1.2054	1.2012	1.1965	1.1899	1518.3	1501.4	1480.7	1465.2
0.1073	1.1783	1.1743	1.1697	1.1635	1512.8	1496.0	1477.0	1459.9
0.2124	1.1517	1.1479	1.1434	1.1377	1506.6	1489.9	1472.4	1453.7
0.2983	1.1298	1.1262	1.1217	1.1163	1501.0	1484.3	1468.0	1447.8
0.3361	1.1202	1.1166	1.1122	1.1069	1498.4	1481.7	1465.9	1445.0
0.4024	1.1031	1.0997	1.0953	1.0903	1493.6	1476.9	1461.9	1439.8
0.4962	1.0788	1.0755	1.0713	1.0665	1486.5	1469.7	1455.8	1431.9
0.5683	1.0599	1.0567	1.0524	1.0479	1480.8	1463.9	1450.8	1425.4
0.6090	1.0491	1.0460	1.0418	1.0374	1477.5	1460.5	1447.8	1421.6
0.6982	1.0252	1.0222	1.0180	1.0138	1470.1	1452.9	1440.9	1412.9
0.7899	1.0003	0.9974	0.9932	0.9892	1462.4	1444.5	1433.5	1403.5
0.8919	0.9721	0.9692	0.9650	0.9611	1453.6	1435.3	1424.9	1392.6
0.9324	0.9607	0.9578	0.9536	0.9497	1450.1	1431.5	1421.3	1388.1
1.0000	0.9415	0.9387	0.9344	0.9306	1444.2	1425.1	1415.3	1380.6
Cyclohexanol (1) + *o*-CA								
0.0000	1.2025	1.1976	1.1930	1.1899	1469.5	1452.6	1435.7	1418.7
0.1024	1.1771	1.1723	1.1679	1.1650	1468.4	1452.3	1437.7	1420.2
0.2022	1.1522	1.1476	1.1435	1.1406	1467.3	1451.9	1438.4	1420.3
0.2981	1.1282	1.1237	1.1200	1.1170	1466.1	1451.0	1438.2	1419.4
0.3390	1.1179	1.1135	1.1099	1.1069	1465.5	1450.5	1438.0	1418.6
0.4016	1.1021	1.0977	1.0943	1.0913	1464.6	1449.6	1437.3	1417.2
0.4986	1.0772	1.0730	1.0699	1.0668	1462.7	1447.7	1435.9	1414.1
0.5681	1.0593	1.0550	1.0521	1.0489	1461.2	1445.9	1434.4	1411.2
0.6010	1.0507	1.0464	1.0435	1.0404	1460.3	1445.0	1433.5	1409.7
0.6994	1.0246	1.0204	1.0176	1.0144	1457.4	1441.6	1430.1	1404.3
0.7987	0.9977	0.9935	0.9909	0.9875	1453.7	1437.2	1425.9	1397.6
0.8992	0.9700	0.9657	0.9631	0.9595	1448.9	1431.7	1420.7	1389.8
0.9318	0.9608	0.9566	0.9539	0.9502	1447.1	1429.8	1418.9	1387.0
1.0000	0.9415	0.9372	0.9344	0.9306	1443.3	1425.1	1414.6	1380.9
Cyclohexanol (1) + aniline (2)								
0.0000	1.0139	1.0079	1.0044	1.0004	1612.8	1606.4	1586.2	1572.6
0.1062	1.0089	1.0040	1.0007	0.9970	1598.5	1591.4	1573.4	1558.6
0.2269	1.0026	0.9985	0.9953	0.9920	1580.8	1572.9	1557.0	1540.4
0.2978	0.9985	0.9947	0.9916	0.9882	1569.9	1561.3	1546.4	1528.7
0.3248	0.9967	0.9931	0.9899	0.9868	1565.6	1556.8	1542.1	1524.0
0.4031	0.9916	0.9884	0.9851	0.9820	1552.9	1543.2	1529.6	1510.0
0.4995	0.9849	0.9819	0.9785	0.9756	1536.6	1525.8	1513.1	1491.7
0.5784	0.9789	0.9760	0.9727	0.9697	1522.9	1511.0	1499.0	1475.9
0.6109	0.9763	0.9736	0.9701	0.9671	1517.1	1504.8	1493.0	1469.1
0.6977	0.9692	0.9665	0.9630	0.9599	1501.4	1487.8	1476.6	1450.6
0.7918	0.9611	0.9584	0.9547	0.9514	1484.0	1468.8	1458.1	1429.7
0.8949	0.9517	0.9489	0.9449	0.9414	1464.4	1447.4	1437.2	1405.8
0.9234	0.9490	0.9462	0.9422	0.9386	1459.0	1441.4	1431.3	1399.1
1.0000	0.9415	0.9387	0.9344	0.9306	1444.2	1425.1	1415.3	1380.6

Note: Standard uncertainties u are, u (T) = ± 0.02 K, u(p) = ± 0.04 MPa and the combined expanded uncertainty Uc in mole fraction, density and sound velocity were Uc (x) = ±0.004, Uc (ρ) = ± 0.003 × 10^{-3} kg·m^{-3} and Uc (u) = ± 0.1 m·s^{-1} respectively (0.95 level of confidence).

the electron density on the amino group making it lesser donation of a lone pair of electrons to a proton.

In the *o*-CA, the chloro group is in ortho position, which can lead to steric hindrance and a slight decrease in basicity when compared to aniline. Whereas, when the chloro group is in *meta* position, it has a reduced effect on the amino group. Hence, more negative V_m^E data was observed in the binary system containing cyclohexanol and *o*-CA aniline when compared to cyclohexanol and *m*-CA system.

Moreover, the group linked to the benzene ring determines the π-electron density in its compounds. As a result, the net concentration of electrons in the ring determines how component molecules interact heteromolecular. The distance between the orientation of the two groups on the benzene ring may have an impact on these chemical reactions. It is anticipated that the bond between molecules would diminish as the distance separating the two groups grows. In the case of an *ortho* isomer, the intermolecular interactions cause a large strain in the ring creating an opposite pole at *ortho* side, developing a dipolar character when compared to *meta* derivatives. Therefore, it was anticipated that interactions would be greater in *ortho* derivatives as opposed to *meta* derivatives [47].

3.2. Excess isentropic compressibility (κ_S^E)

Table S1 shows reports the excess molar isentropic compressibility (κ_S^E) various temperatures of all the binary liquids combinations of different mole fractions. Applying Eq. (4), the isentropic compressibility (κ_S) was successfully determined.

$$\kappa_S = \left(\rho \cdot u^2\right)^{-1} = V_m \left(M \cdot u^2\right)^{-1} \quad (4)$$

where M is the combination's molar mass and molar isentropic compressibility is $K_{S,m.}$ The results were determined using the proposed relations by Douheret *et al.* [48,49].

Table 4
Parameters (A_i) of Eq. (1) for densities and speed of sound of cyclohexanol with aniline and chloro substituted anilines at different temperautres.

$F(x)$	T/K	A_1	A_2	A_3	σ
Cyclohexanol (1) + *m*-chloro aniline (2)					
$\rho \times 10^{-3}$/kg·m^{-3}	303.15	1.204	−0.245	−0.017	0.0004
	308.15	1.201	−0.241	−0.021	0.0003
	313.15	1.195	−0.230	−0.028	0.0006
	318.15	1.189	−0.201	−0.037	0.0005
u/m·s^{-1}	303.15	1518.0	−55.4	−19.8	0.3
	308.15	1501.0	−52.5	−24.7	0.3
	313.15	1481.0	−36.1	−30.2	0.2
	318.15	1465.0	−50.9	−34.8	0.3
Cyclohexanol (1) + *o*-chloro aniline (2)					
$\rho \times 10^{-3}$/kg·m^{-3}	303.15	1.203	−29.910	0.037	0.0004
	308.15	1.198	−30.570	0.043	0.0005
	313.15	1.195	−31.480	0.053	0.001
	318.15	1.194	−32.680	0.064	0.001
u/m·s^{-1}	303.15	1461.0	−10.3	−7.2	0.2
	308.15	1456.8	−32.6	0.4	0.2
	313.15	1437.0	−24.1	0.7	0.2
	318.15	1420.0	−43.7	3.2	0.3
Cyclohexanol (1) + aniline (2)					
$\rho \times 10^{-3}$/kg·m^{-3}	303.15	1.013	−0.044	−0.028	0.0001
	308.15	1.008	−0.035	−0.034	0.0002
	313.15	1.004	−0.034	−0.036	0.0002
	318.15	1.001	−0.031	−0.036	0.0002
u/m·s^{-1}	303.15	1613.3	−137.4	−32.2	0.3
	308.15	1606.9	−142.3	−40.0	0.3
	313.15	1586.1	−123.1	−49.2	0.4
	318.15	1573.2	−133.4	−59.9	0.4

$$K_{S,m} = -(\delta V_m/\delta P)_s = V_m \kappa_S = \sum x_i M_i \Big/ (\rho u)^2 \tag{5}$$

After calculating the surplus molar amounts,

$$K^E_{S,m} = K_{S,m} - K^{id}_{S,m} \tag{6}$$

where $K^{id}_{S,m}$ has been determined using the Benson and Kiyohara method [50]:

$$K^{id}_{S,m} = \Sigma x_i \left\{ K^*_{S,i} - T A^*_{P,i} \left[\left(\frac{\Sigma x_i A^*_{P,i}}{\Sigma x_i C^*_{P,i}} \right) - \left(\frac{A^*_{P,i}}{C^*_{P,i}} \right) \right] \right\} \tag{7}$$

While the aforementioned equations, $A^*_{P,i}$ is the product of the molar volume $V^*_{m,i}$, $\alpha^*_{P,i}$ is the isobaric expansivity, $C^*_{P,i}$ is the isobaric molar heat capacity, and $K^*_{S,i}$ is the properties of the pure liquid component *i*.

The statistics on excess isentropic compressibility are displayed in Fig. 2, over the entire composition temperature range at $T = 303.15$ K for the mixtures of cyclohexanol with aniline, *ortho*-chloroaniline and *meta*-chloroaniline. The (κ^E_S) data, can be described by two opposing elements, which are (i) loss of reversible dipolar coupling, size and shape differences between different molecules and (ii) electron-donor-acceptor interactions, dipole-dipole, dipole-induced dipole, and intervening accommodation of aniline, *ortho*-chloroaniline and *meta*-chloroaniline in cyclohexanol matrix. The former factor leads to an increase of free length measured as proposed by Jacobson [51]. This causes negative deviation in sound velocity and positive deviations in excess isentropic compressibilities, the latter effect conversely creates positive variance in sound velocity and negative variance in (κ^E_S). The actual deviation depends on the proportional amount, sign, and strength of the two opposing impacts [52]. A perusal of curves in Fig. 2 reveal that the factors which are responsible for negative deviation in excess compressibility are predominate in using the all binary combination. The algebraic κ^E_S data for the mixtures of cyclohexanol with aniline, *ortho*-chloroaniline, and *meta*-chloroaniline fall in the order: aniline > *o*-chloroaniline > *m*-chloroaniline

3.3. Excess properties of free length (L^E_f) acoustical impedance (Z^E) speed of sound (u^E)

The u can also be used to infer different features from it, which can be used to describe the kind and intensity of interaction that exists between the components. The specifications such as intermolecular free length (L_f) [51], which is a measure of free space accessible inside the arrangements of molecules, and specific acoustic imped ance (Z) were estimated using the following relation [51,53].

$$L_f = K \Big/ \left(u \cdot \rho^{1/2} \right) \tag{8}$$

$$Z = u \cdot \rho \tag{9}$$

where L_f is the free length of ideal binary mixing, K is a temperature dependence of constant value of $\{=(93.875 + 0.375T) \times 10^{-8}\}$ [51]). The excess functions operations of intermolecular interaction of free length L_f and acoustic impedance Z were computed utilizing the relations:

$$L^E_f = L_f - \sum x_i L^*_{f,i} \tag{10}$$

$$Z^E = Z - \sum x_i Z^*_i \tag{11}$$

$$u^E = u - \sum x_i u_i \tag{12}$$

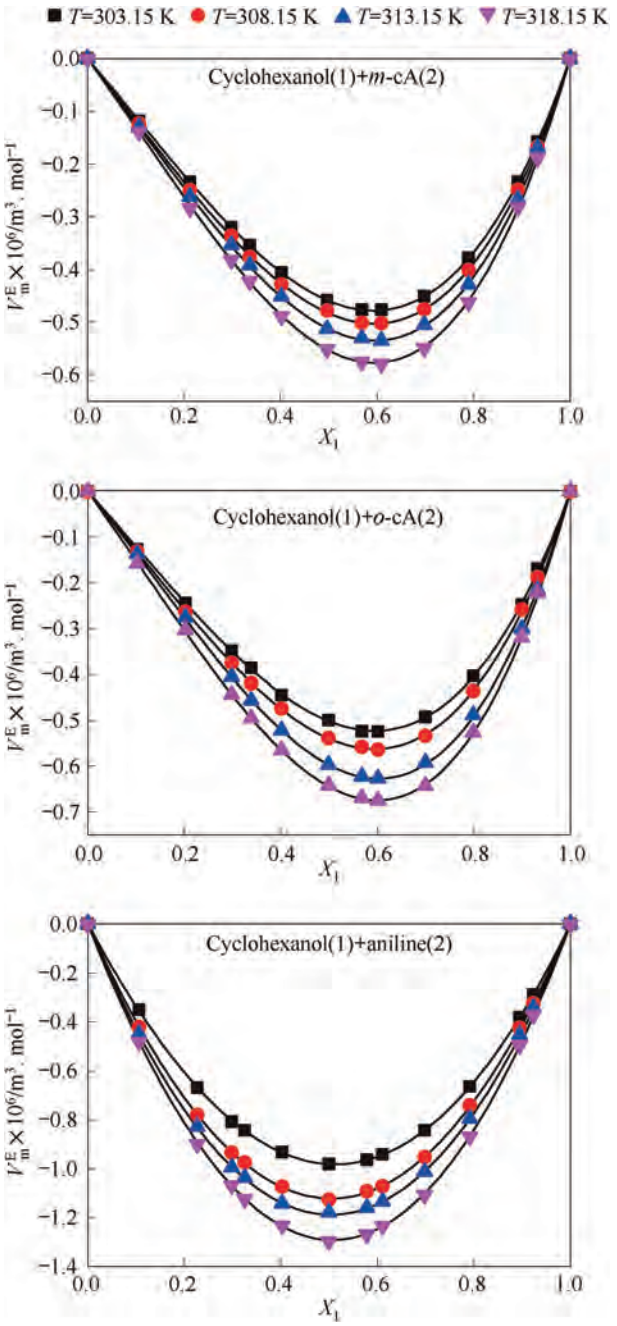

Fig. 1. Excess molar volume of binary mixtures containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at different temperatures.

The results of K_S^E, L_f^E and Z^E were further fitting to a polynomial equation resembling that of the extra molar volume.

The intermolecular interaction of free length is a one of the significant physical attributes of binary liquid mixtures, which mostly influences the sound velocity in liquids. The densely packed molecules that cause the negative excess functions explain the predominant effective molecular interactions between component molecules, when they are mixed. The sign of K_S^E and L_f^E may play key role in assessing the bonding of hydrogen and the creation of charge transfer complexes between interaction molecules in binary liquid mixtures, dipole-dipole interactions, dipole-induced dipole interactions followed by Refs. [54,55] causing negative values of L_f^E. An analysis of L_f^E slopes show in Fig. 3. Suggest that, specific interactions are prevailing between cyclohexanol with aniline, *o*-chloroaniline and *m*-chloroaniline binary mixtures. The Z^E (Fig. 4) values indicate positive for every system at every temperature that was examined. The combination of mixture shows how the interactions between the mixture's dissimilar molecules are becoming stronger.

A look at the curves in Fig. 5 suggests the excess speed of sound (u^E) statistics data are positive for the cyclohexanol with aniline, *ortho*-chloroaniline and *meta*-chloroaniline binary liquid mixes at every temperature under investigation over the whole composition range. The extent and indication of u^E provides the following information about the specific intermolecular interactions prevailing in the binary liquid mixtures.

Generally positive deviations speeds of sound u^E indicate the presence of tightly bonded interactions and negative deviation in u^E specify weakly bonded interactions between unlike molecules in the binary mixtures [56,57]. The studied similar molecules' positive u^E data in the binary mixes.

3.4. Prigogine flory patterson (PFP)

The Prigogine-Flory-Patterson (PFP) analytical method for non-electrolyte combinations of liquids could be used to appropriately analyzed the information being studied. [58–60]. Nevertheless, liquid mixtures and non-associated liquids are not covered by the PFP hypothesis. But in liquid mixes, where one or both constituents are pure and interact with one another because of differences in their chemical makeup, size, and form, the issue gets more complicated. Keeping this in mind, the V_m^E data were evaluated using PFP theory to investigate its capacity to predict of isentropic compressibilities and sound velocity in a variety of binary liquid combinations containing cyclohexanol + aniline and chloro substituted anilines. Here, the PFP simulation was implemented using the preceding outlined procedure and formulae [61]. Furthermore, PFP theory can be used to polar and non-polar molecules that are mixed together in a binary combination.

$$\frac{V_m^E}{(X_1V_1^* + X_2V_2^*)} = \underbrace{\frac{\left(\tilde{V}^{1/3}-1\right)\tilde{V}^{2/3}\Psi_1\theta_1\chi_{12}}{\left[\left(\frac{4}{3}\right)\tilde{V}^{-1/3}-1\right]P^*}}_{\text{(int. contribution)}} - \underbrace{\frac{\left(\tilde{V}_1-\tilde{V}_2\right)^2\left[\left(\frac{14}{9}\right)\tilde{V}^{-1/3}-1\right]\Psi_1\Psi_2}{\left(\frac{4}{3}\right)\tilde{V}^{-1/3}-1}}_{\text{(fv. contribution)}} + \underbrace{\frac{\left(\tilde{V}_1-\tilde{V}_2\right)(P_1^*-P_2^*)\Psi_1\Psi_2}{P_1^*\Psi_1+P_2^*\Psi_2}}_{(P^*.\ \text{contribution})} \tag{13}$$

where V and V_i were the reduced volumes of mixture and pure components; V_i^* and P_i^* were the characteristic volume and pressure of pure components Ψ_i and θ_i represents contact energy fraction and surface fraction of pure components respectively.

Table 6 shows the several of the PFP theory's variables for applying pure components. Using the PFP theoretical terms, the contact interactions variable is calculated. χ_{12} for each liquid mixture based on excess molar volume equimolar values at $x_1 = 0.5$. Table 7 shows and measure that the only positive contribution to excess molar volume of P^*, whereas the interaction and free volume

Table 5
Coefficients (a_i) of equation (3) and standard deviation σ for excess properties of binary mixtures at different temperatures.

$F(x)$	T/K	a_1	a_2	a_3	σ
Cyclohexanol (1) + *m*-chloro Aniline (2)					
$V_m^E \times 10^6/m^3 \cdot mol^{-1}$	303.15	−1.778	0.496	−0.11	0.0004
	308.15	−1.834	0.481	0.081	0.0006
	313.15	−1.998	0.451	−0.111	0.001
	318.15	−2.109	0.378	−0.217	0.001
$K_S^E \times 10^{10}/TPa^{-1}$	303.15	−97.68	−14.99	−0.332	0.001
	308.15	−106.3	−24.81	−0.826	0.001
	313.15	−128.8	−21.70	−0.093	0.001
	318.15	−196.0	11.56	77.79	0.001
$10^3 Z^E/kg \cdot m^{-2} \cdot s^{-1}$	303.15	−51.17	−5.567	−0.605	0.008
	308.15	−71.54	−20.22	2.71	0.02
	313.15	−82.99	−31.89	−3.479	0.03
	318.15	−10.44	−32.31	5.154	0.1
$10^2 L_f^E/nm$	303.15	−0.051	0.002	0.001	0.0005
	308.15	−0.021	0.045	0.004	0.0004
	313.15	0.036	0.403	0.047	0.0004
	318.15	0.029	0.084	0.006	0.0001
$u^E/m \cdot s^{-1}$	303.15	13.46	84.64	32.24	0.006
	308.15	14.51	102.7	40.03	0.001
	313.15	17.14	108.2	39.55	0.01
	318.15	19.60	115.6	77.79	0.004
Cyclohexanol (1) + *o*-CA (2)					
$V_m^E \times 10^6/m^3 \cdot mol^{-1}$	303.15	−7.513	2.816	−0.222	**0.0001**
	308.15	−7.74	2.850	−0.191	**0.0004**
	313.15	−7.913	2.952	−0.236	**0.0001**
	318.15	−8.881	2.862	−0.151	**0.0002**
$K_S^E \times 10^{10}/TPa^{-1}$	303.15	−22.08	2.847	−0.56	**0.02**
	308.15	−27.42	−5.36	−0.458	**0.005**
	313.15	−33.66	−9.042	−1.332	**0.02**
	318.15	−22.08	−2.847	−0.356	**0.003**
$10^3 Z^E/kg \cdot m^{-2} \cdot s^{-1}$	303.15	27.56	−3.215	−0.854	0.01
	308.15	37.36	−0.748	−2.137	0.05
	313.15	55.94	6.207	−3.638	0.03
	318.15	68.95	0.03	−3.146	0.01
$10^2 L_f^E/nm$	303.15	−0.226	−0.164	−0.001	0.0001
	308.15	−0.256	−0.026	0.001	0.0001
	313.15	−0.287	−0.43	0.003	0.0001
	318.15	−0.347	−0.044	0.003	0.0001
$u^E/m \cdot s^{-1}$	303.15	19.91	−7.435	0.041	0.01
	308.15	24.75	−5.916	−0.595	0.04
	313.15	30.16	−5.483	−0.32	0.003
	318.15	34.78	−6.61	−4.14	0.01
Cyclohexanol (1) + aniline (2)					
$V_m^E \times 10^6/m^3 \cdot mol^{-1}$	303.15	−3.925	−0.189	0.069	0.001
	308.15	−4.493	−0.083	−0.104	0.001
	313.15	−4.753	−0.074	−0.698	0.004
	318.15	−5.174	−0.164	−0.106	0.001
$K_S^E \times 10^{10}/TPa^{-1}$	303.15	−0.665	−0.033	0.002	0.0001
	308.15	−0.78	−0.048	−0.481	0.0001
	313.15	−0.884	−0.047	−0.013	0.0004
	318.15	−1.052	−0.089	−0.02	0.0001
$10^3 Z^E/kg \cdot m^{-2} \cdot s^{-1}$	303.15	62.41	13.17	2.1320	0.2
	308.15	78.19	17.01	2.9930	0.2
	313.15	90.23	−20.28	5.6410	0.3
	318.15	90.23	−20.28	5.6410	0.1
$10^2 L_f^E/nm$	303.15	−0.231	0.001	−0.009	0.001
	308.15	−0.282	−0.001	−0.011	0.001
	313.15	−0.315	0.004	−0.016	0.001
	318.15	−0.389	−0.01	−0.021	0.001
$u^E/m \cdot s^{-1}$	303.15	31.87	−7.106	1.624	0.1
	308.15	39.67	−7.086	1.579	0.1
	313.15	48.86	−9.635	2.449	0.1
	318.15	59.61	−8.805	3.273	0.1

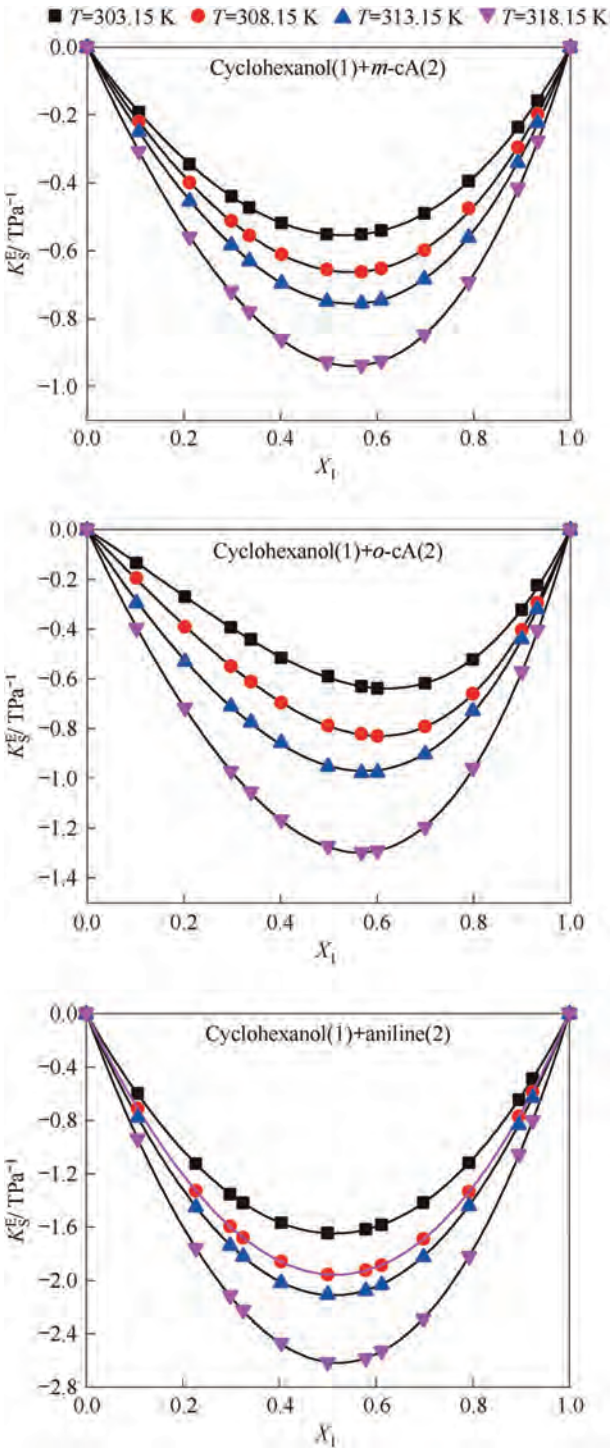

Fig. 2. Excess isentropic compression of binary mixtures containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at different temperatures.

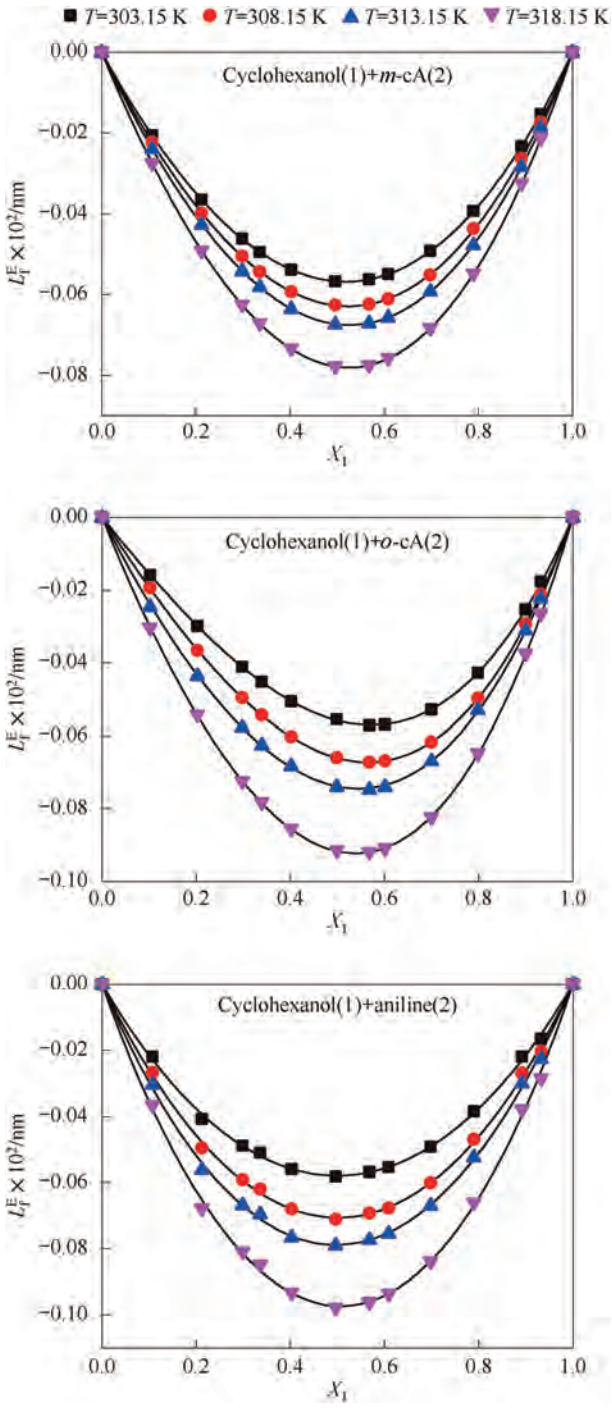

Fig. 3. Excess intermolecular free length of binary mixtures containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at different temperatures.

contributions are negative. Both of these elements are dominant over P^* contribution. The substantially higher negative values of the χ_{12} parameter for the tested systems indicate a higher likely hood of chemical interaction, as demonstrated by the results V_m^E. Fig. 6 shows a comparison between the measured excess molar volume and the mathematically predicted excess molar volume at $T = 303.15$ K using PFP concept. There is a strong link between the data displayed in the image.

Studying the speed of sound (u) theoretically and applying different ideas proves the cessation of intermolecular interactions as determined by various calculated factors [62]. The work discussed involved the theoretical evaluation of binary liquid mixes of various temperature (T = 303.15, 308.15, 313.15, and 318.15 K) by the applied of two theoretical model: (i) collision frequency theory (CFT) [63]. (ii) Intermolecular free length theory (FLT) [51]. The equations' specifics were already made public [44]. To evaluate their amendment factor, we used the to get the average standard

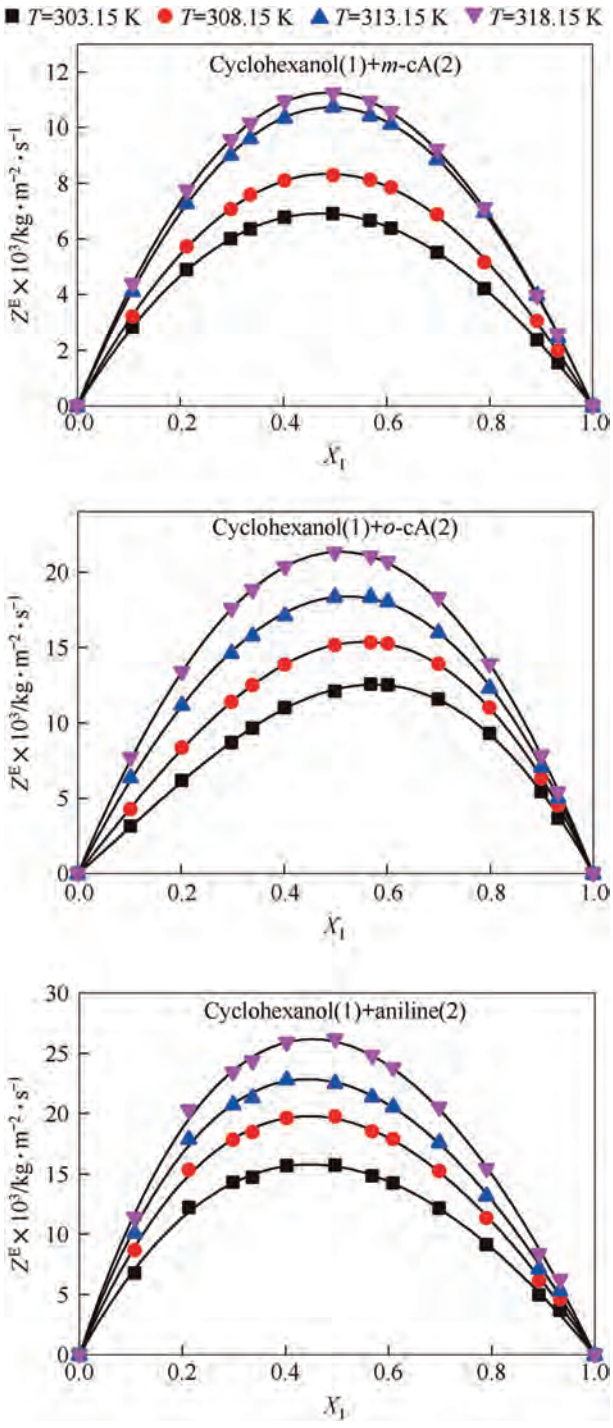

Fig. 4. Excess specific acoustic impedance of binary mixtures containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at different temperatures.

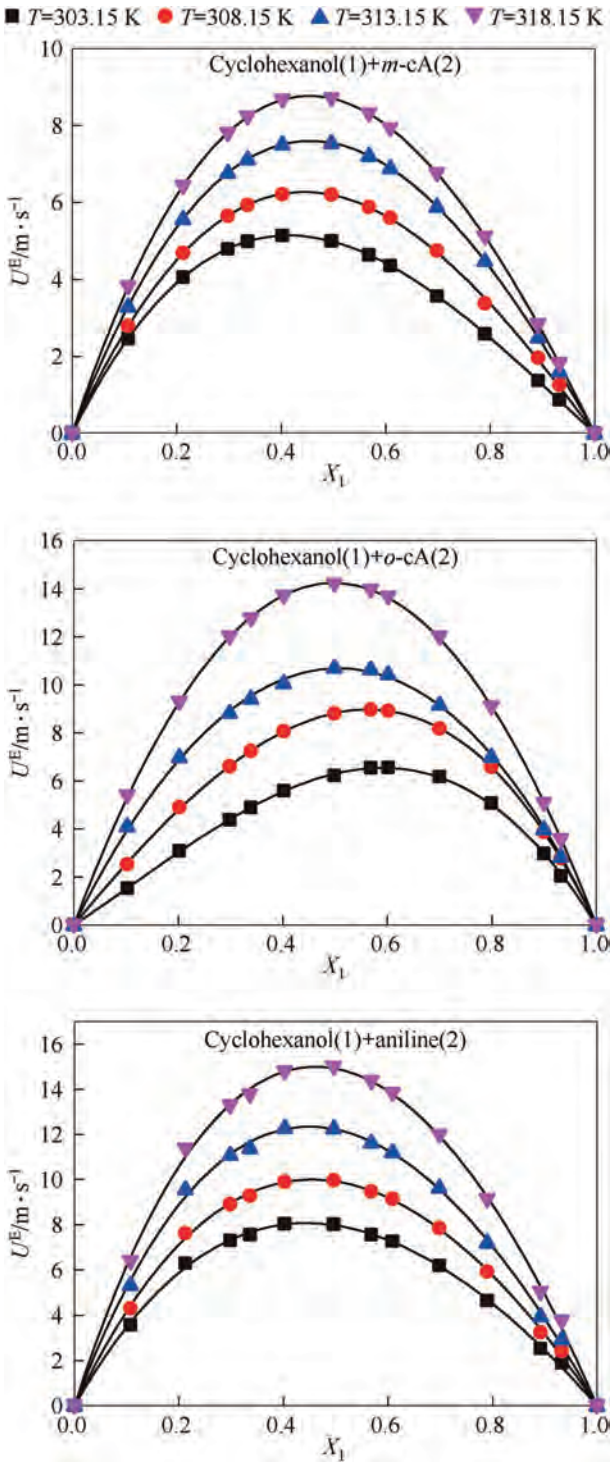

Fig. 5. Excess speeds of sound of binary mixtures containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at different temperatures.

square variance (σ) between the experimental and theoretical results, use the following equation:

$$\sigma = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_{exp.} - Y_{theor.}}{Y_{exp.}}\right)\right]^{1/2} \quad (14)$$

The results for average standard square variance values have been assembled in Table S5. The speed of sound of liquid mixture is a significant property at various applications, including material science, chemistry, and process engineering. Accurate predictions help in designing and controlling processes. Choosing the appropriate theoretical model (in this case, CFT and FLT) based on RMSD results ensures more reliable predictions and can lead to better understanding and control of mixture behaviours.

4. Excess Partial Characteristics

The partial molar characteristics (partial molar volume and partial molar compression, Eq. (15)) using cyclohexanol with aniline and chloro substituted anilines (Eq. (12)) components in this mixture were estimated using the following equation [64] for the whole composition range.

$$\overline{Y}_{m,1} = Y^{E}_{m} + Y^{*}_{m,1} + x_2\left(\partial Y^{E}_{m}\Big/\partial x_1\right)_{T,P} \quad (15)$$

$$\overline{Y}_{m,2} = Y^{E}_{m} + Y^{*}_{m,2} + x_1\left(\partial Y^{E}_{m}\Big/\partial x_1\right)_{T,P} \quad (16)$$

where Y^{*}_{m1} and Y^{*}_{m2} are the molar volumes of each component, cyclohexanol with aniline and chloro substituted anilines, respectively. The variation, $\left(\partial P^{E}_{m}/\partial x_1\right)_{T,p}$ in Eqs. (15) and (16) were obtained by differentiating Eq. (3), which results in the following equations for $\overline{Y}_{m,1}$ and $\overline{Y}_{m,2}$

$$\tilde{Y}_{m,1} = Y^{*}_{m,1} + x_2^2\sum_{i=0}^{j}A_i(1-2x_1)^i - 2x_1x_2^2\sum_{i}^{j}A_i i(2x_1)^{i-1} \quad (17)$$

$$\tilde{Y}_{m,2} = Y^{*}_{m,2} + x_1^2\sum_{i=0}^{j}A_i(1-2x_1)^i - 2x_1^2x_2\sum_{i=1}^{j}A_i i(1-2x_1)^{i-1} \quad (18)$$

Making use of the partial molar characteristics values, $\overline{Y}^{\circ}_{m,1}$ and $\overline{Y}^{\circ}_{m,2}$ at infinite dilution obtained from Eqs. (15)–(18), the excess partial molar characteristics, $\overline{Y}^{\circ E}_{m,1}$ and $\overline{Y}^{\circ E}_{m,2}$ at infinite dilution are calculated by using the following relations:

$$\overline{Y}^{\circ E}_{m,1} = \left(\overline{Y}_{\cdot m,1} - Y^{*}_{1}\right) \quad (19)$$

$$\overline{Y}^{\circ E}_{m,2} = \left(\overline{Y}_{\cdot m,2} - Y^{*}_{2}\right) \quad (20)$$

Added to that, a different approach that makes use of the apparent molar properties was successfully used to calculate the partial properties of molar volume at a constant dilution of $Y_{\phi,1}$ and $Y_{\phi,2}$ for the mixtures of two components are determined using the following equations [65–67].

$$Y_{\phi,1} = Y^{*}_{m}, 1 + \left(Y^{E}_{m}\Big/x_1\right) \quad (21)$$

$$Y_{\phi,2} = Y^{*}_{m}, 2 + \left(Y^{E}_{m}\Big/x_2\right) \quad (22)$$

Eqs. (21) and (22) make it simple to calculate the apparent molar characteristics using the matching mole fractions and experimental V^{E}_{m} values and corresponding mole fractions. Using the linear regression of $\overline{Y}^{\circ}_{\phi,1}$ versus. X_1 for dilute solutions of cyclohexanol in aniline and chloro substituted anilines and $Y_{\phi,2}$ *versus* X_2 for dilute solution of aniline and chloro substituted anilines in cyclohexanol, the values of limiting apparent (or partial) molar properties, $\overline{Y}^{\circ}_{\phi,1}$ and $\overline{Y}^{\circ}_{\phi,2}$ at endless diluting have been acquired. Those can be referred to as partial molar properties at endless diluting, represented as $\overline{Y}^{\circ}_{m,1}$ and $\overline{Y}^{\circ}_{m,2}$ earlier. The values of $\overline{Y}^{\circ E}_{\phi,1}$ and $\overline{Y}^{\circ E}_{\phi,2}$ are used for this calculation.

The values for $\overline{V}^{\circ}_{m,1}$, $\overline{V}^{\circ}_{\phi,1}$, V^{*}_{1}, $\overline{V}^{E}_{m,1}$, $\overline{V}^{\circ E}_{\phi,1}$, $\overline{V}^{\circ}_{m,2}$, $\overline{V}^{\circ}_{\phi,2}$, V^{*}_{2}, $\overline{V}^{E}_{m,2}$ and $\overline{V}^{\circ E}_{\phi,2}$ for all the three different binary liquid systems in various temperatures are listed on Table S3 and Fig. 7(a),(b). A careful observation of $\overline{V}^{\circ E}_{\phi,1}$, $\overline{V}^{\circ E}_{\phi,2}$ and $\overline{V}^{E}_{m,2}$ are negative across the board for all binary liquid combinations (mol fraction) composition range. This indicate that the molar volume of each component in the pure state. In general, the negative $\overline{V}^{\circ E}_{\phi,1}$, $\overline{V}^{\circ E}_{\phi,2}$ and $\overline{V}^{E}_{m,2}$ values indicate the presence of an observable a solute-solvent combination of dissimilar molecules [68]. While the positive $\overline{V}^{E}_{m,1}$ the existence of weak solute-solvent interaction. When the latter's construction approaches zero, the aforementioned parameters, which are sensitive to solute-solvent interaction, alter the situation in the solvent by solute. In general, it is suggested that the negative partial molar volume of a solute at infinite dilution indicate a large volume decrease when added to pure solvent [69,70]. The infinite dilution $\overline{V}^{E}_{m,1}$ and $\overline{V}^{\circ}_{m,2}$ above data is an indication of strong interaction are prevailing between studied components of cyclohexanol in aniline and chloro substituted anilines binary liquid mixtures. The negative

Table 6
The values of reduced volume, $\tilde{V}$, characteristic volume, V^{*}, characteristic pressure, P^{*} characteristic temperature, T^{*}, isothermal compressibility, κ_T, isentropic compressibility, κ_S and thermal expansion coefficient, α of pure liquids at temperatures, $T = (303.15$ to $318.15)$ K.

T/K	$\tilde{V}$	$10^6V^{*}/m^3\cdot mol^{-1}$	$10^{-8}P^{*}/J\cdot cm^{-3}$	T^{*}/K	$10^{10}K_T/m^2\cdot N^{-1}$	10^{10} $K_S/m^2\cdot N^{-1}$	$10^4\alpha/K^{-1}$
Cyclohexanol							
303.15	1.2481	83.9836	6.6665	5313	5.7144	3.8934	9.8554
308.15	1.2518	84.0438	6.6972	5348	5.7830	3.9368	9.8682
313.15	1.2564	84.0176	6.7694	5370	5.9612	4.0588	9.9292
318.15	1.2609	83.9535	6.7231	5395	6.1158	4.1666	9.9790
m-CA							
303.15	1.2667	83.9836	8.1449	5068	7.8506	5.0987	10.7601
308.15	1.2716	84.0438	8.2394	5091	8.0538	5.2538	10.8254
313.15	1.2758	84.0176	8.2340	5123	8.1745	5.3480	10.8569
318.15	1.2820	85.0282	8.2527	5133	8.5424	5.6351	10.9841
o-CA							
303.15	1.2666	83.988	8.9548	5372	5.0924	7.8426	10.7567
308.15	1.2715	83.921	8.9756	5396	5.2456	8.0383	10.8197
313.15	1.2757	84.021	8.9668	5416	5.3428	8.1678	10.8542
318.15	1.2820	83.952	8.9773	5440	5.6376	8.5454	10.9853
Aniline							
303.15	1.2497	73.500	9.0188	5291	5.2131	3.7917	9.9306
308.15	1.2535	73.715	9.0997	5324	5.2958	3.8450	9.9522
313.15	1.2581	73.700	9.1126	5347	5.4443	3.9572	10.009
318.15	1.2623	73.749	9.1591	5375	5.5615	4.0421	10.047

Table 7
Values of χ_{12}, V_m^E experimental and calculated (using PFP theory) and three PFP contributions for near equimolar composition at temperatures, $T = 303.15$ to 318.15 K.

T/K	$\chi_{12} \times 10^{-8}$/J·mol^{-1}	$V_m^E \times 10^6$/m^3·mol^{-1}		PFP contribution to (V_m^E)		
		Expt.	PFP	int.	Fv	P^*
Cyclohexanol (1) + m-CA (2)						
303.15	−454	−0.4770	−0.4709	−0.4769	−0.0001	0.0061
308.15	−468	−0.5014	−0.5013	−0.5014	−0.0003	0.0003
313.15	−486	−0.5312	−0.5315	−0.5311	−0.0010	0.0006
318.15	−509	−0.5745	−0.5748	−0.5743	−0.0012	0.0006
Cyclohexanol (1) + O-chloro aniline (2)						
303.15	−469	−0.5229	−0.5195	−0.5228	−0.0001	0.0034
308.15	−492	−0.5574	−0.5574	−0.5574	−0.0002	0.0002
313.15	−540	−0.6231	−0.6234	−0.6230	−0.0007	0.0003
318.15	−563	−0.6700	−0.6704	−0.6699	−0.0009	0.0004
Cyclohexanol (1) + aniline (2)						
303.15	−971	−0.9819	−0.9771	−0.9818	−0.0001	0.0047
308.15	−1098	−1.1273	−1.1271	−1.1272	−0.0002	0.0003
313.15	−1128	−1.1800	−1.1800	−1.1799	−0.0006	0.0005
318.15	−1206	−1.2945	−1.2945	−1.2944	−0.0007	0.0006

values of excess partial molar volume indicate the contraction in the volume of mixtures due to charge transfer, complex formation between component molecules and also molecule interaction among unlike molecules is stronger than of like molecules.

Different value of $K^{\circ}_{m,1}$, $\overline{K}^{\circ}_{\phi,1}$, K^{*}_{1}, $\overline{K}^{E}_{m,1}$, $\overline{K}^{\circ E}_{\phi,1}$, $\overline{K}^{\circ}_{m,2}$, $\overline{K}^{\circ}_{\phi,2}$, K^{*}_{2}, $\overline{K}^{E}_{m,2}$ and $\overline{K}^{\circ E}_{\phi,2}$ as binary function of mol fraction x_1 of cyclohexanol and Various temperatures are provided in Table S4. An analysis curves of Fig. 7 (c), (d) suggested that the value $\overline{K}^{E}_{m,1}$, $\overline{K}^{E}_{m,2}$, $\overline{K}^{\circ E}_{\phi,1}$ and $\overline{K}^{\circ}_{\phi,2}$ for both the binary liquid combination with each component's indication and the overall composition range in the mixture are less than their corresponding of compressibility of excess molar isentropic in its pure condition. Further $\overline{K}^{E}_{m,1}$, $\overline{K}^{E}_{m,2}$, $\overline{K}^{\circ E}_{\phi,1}$ and $\overline{K}^{\circ}_{\phi,2}$ can be explained in terms of structure and geometrical compressibility as proposed by Hall [71] and by others [72,73] structural compressibility a raised from the rupture of associated structure of component molecules and geometrical compressibility is due to side by side composition of molecular contracting the amount of space and lowering the average spacing between molecules.

5. Investigated of Density Functional Theory (DFT)

The DFT calculations, several criteria are typically used to identify and quantify hydrogen bonds of interaction energies (ΔE)

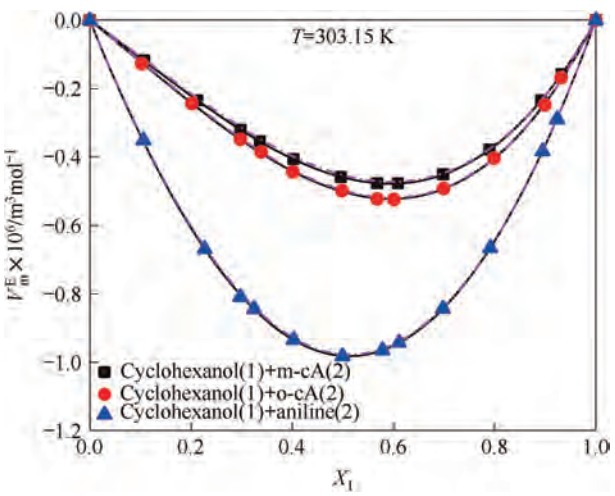

Fig. 6. Comparison of experimental excess molar volume and theoretically calculated (by applying PFP (———) for binary mixtures containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at 303.15 K.

of hydrogen-bonded complex binary mixes were computed using the difference between the component molecule's total energy and the energy of the hydrogen-bonded complex, as follows:

$$\Delta E = E_{\text{complex}} - \sum E_{\text{component}} \tag{23}$$

The maximum energies of the complex with hydrogen bonds and individual component molecules are denoted by E_{complex} and $E_{\text{component}}$ respectively. The counterpoise method is used to correct binding strengths regarding the fundamental set superposition inaccuracy [74]. In addition, this offers important details on the variations in the bonding and antibonding orbitals' charge densities as well as those of the proton donor and acceptor. Below are the stabilization energies E (23) linked to hydrogen bonding between sites i and j for each donor and acceptor:

$$E(23) = q_i \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_j}$$

where the diagonal components associated with are ε_i and ε_j, and q_i is the ith donor orbital frequency. For different intermolecular interactions hydrogen bonding complex systems, the equilibrium energy between the anti-bonding orbital components (π^*) of the proton donor and the lone pair electrons (n) of the proton acceptor was calculated [75–78].

In quantum chemistry as well as optical and electric properties, the most important are the highest-occupied molecular orbitals (HOMO) and Lowest-lying unoccupied molecular orbitals (LUMO) [78–80]. The HOMO represents the capacity to provide an electron, whereas the LUMO, an electron acceptor, represents the capacity to receive an electron. The amount of energy gap between the molecular structures HOMO and LUMO determines its Ionization Potential (I), The highest ionization potential (5.872 eV) and electron affinity (0.810 eV) suggest that the aniline complex is the hardest to ionize and the strongest electron acceptor. Electron affinity (A), electrophilicity (ω), chemical potential (μ), electronegativity (χ), chemical hardness (η), and chemical softness (S), its higher chemical hardness (2.531 eV) and lower chemical softness (0.197) further support its greater resistance to electron density changes, confirming its stability [81,82]. Overall, cyclohexanol + aniline forms the most stable complex, while cyclohexanol + m-CA and cyclohexanol + o-CA are more chemically reactive and softer, suggesting they may participate more readily in electron exchange processes. These insights are important for understanding the potential applications of these complexes in chemical systems. We performed computations in utilizing for B3LYP/6-31++G (d, p) and

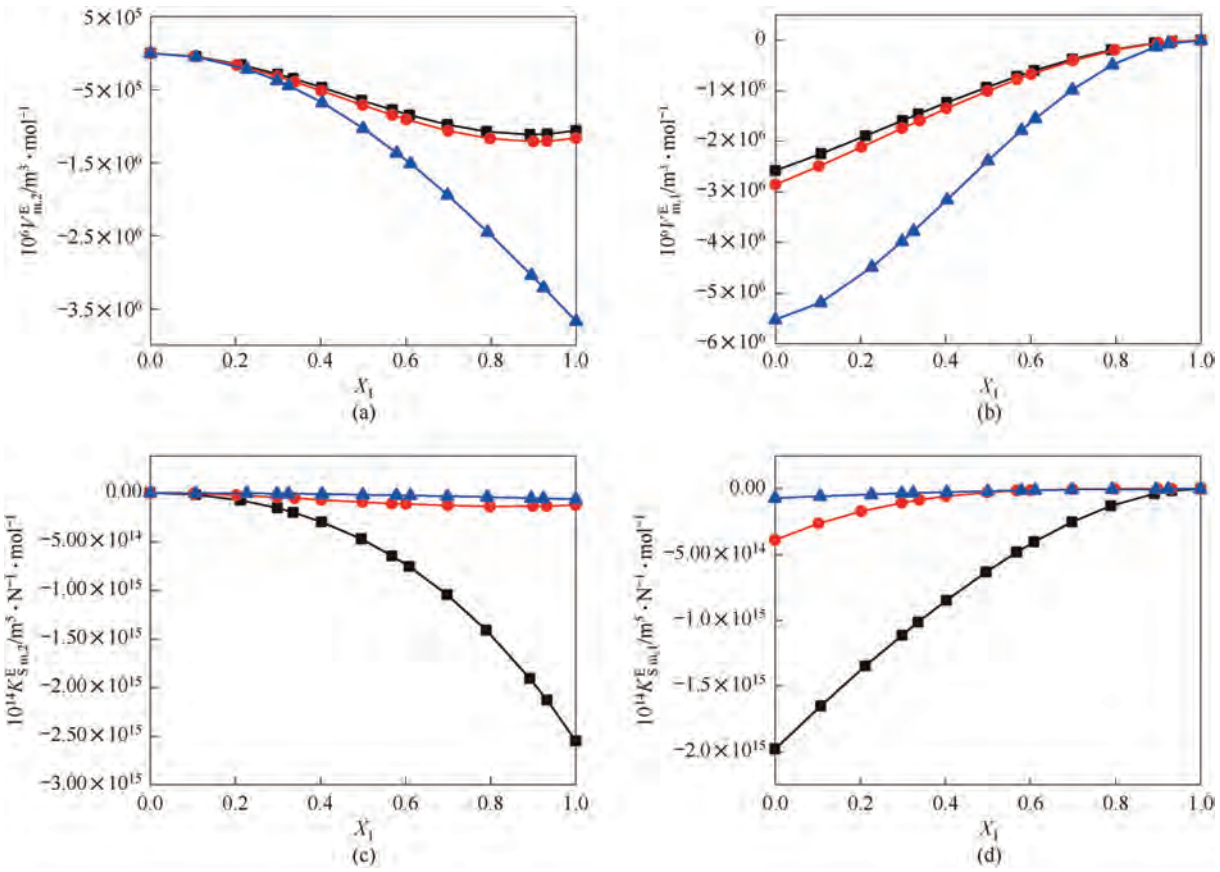

Fig. 7. Excess partial molar volumes (a), (b) and excess partial molar isentropic compressibility (c), (d) over the entire range of composition for the binary mixture containing cyclohexanol (1) + aniline and chlorosubstituted anilines (2) at 303.15 K.

are displayed in Table 8. Using the same software, 3D graphs of the HOMO, LUMO, and orbital components were produced B3LYP/6-31G++ (d, p) level for cyclohexanol with aniline and chloro substituted anilines molecule are illustrated in Fig. 8 (cyclohexanol + aniline, cyclohexanol + *ortho*-chloroaniline, and cyclohexanol + *meta*-chloroaniline.). The red denotes the positive phase while green denotes the negative phase. The graphic makes it evident that the LUMO is centered on the benzene ring, but the HOMO is distributed throughout practically the whole structure. The majority of the orbital components in the HOMO and LUMO are of the π-*anti*-bonding kind. The energy output computed for HOMO is −5.872, −5.487 and −5.448 in cyclohexanol + aniline, cyclohexanol + *ortho*-chloroaniline, and cyclohexanol + *meta*-chloroaniline, respectively. LUMO is −0.810, −0.701 and −0.668 in cyclohexanol + aniline, cyclohexanol + *ortho*-chloroaniline, and cyclohexanol + *meta*-chloroaniline, respectively. The finding of energy gap value (Δ*E*) between the HOMO and LUMO for −5.062, −4.786 and −4.780 in, respectively. The energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the molecule, When the molecule transitions from the organic solvent–solvent phase, the energy gap between the HOMO and LUMO increases [83–86]. There is an electron density exchange during the HOMO to LUMO transformation. This transformation is from chlorine and partially from the ring structure to the ring itself. The LUMO is significantly stabilized due to the strong electron-acceptor nature of an electron-acceptor group within the molecule. This stabilization of the LUMO leads to a lowering of the HOMO–LUMO energy band gap and addition information of molecular hydrogen bonding interactions bond length given by supplementary data and Fig. S3.

Table 8
Calculated quantum chemical parameters of cyclohexanol + *m*-chloroaniline (*m*-CA), cyclohexanol + *o*-chloroaniline (*o*-CA), and cyclohexanol + aniline complexes at B3LYP/6–311 G (d,p) level of theory.

S. No	Chemical parameters	Cyclohexanol + *m*-CA	Cyclohexanol + *o*-CA	Cyclohexanol + aniline
1	Homo value (H)	−5.448	−5.487	−5.872
2	Lumo value (L)	−0.668	−0.701	−0.810
3	Energy gap (ΔE)	−4.780	−4.786	−5.062
4	Ionization potential (I)	5.448	5.487	5.872
5	Electron affinity (A)	0.668	0.705	0.810
6	Electrophilicity (ω)	2.005	2.009	2.205
7	Chemical potential (μ)	−3.091	−3.097	−3.341
8	Electronegativity (χ)	3.086	3.094	3.341
9	Chemical hardness (Ƞ)	2.389	2.395	2.531
10	Chemical softness (S)	2.207	2.201	0.197

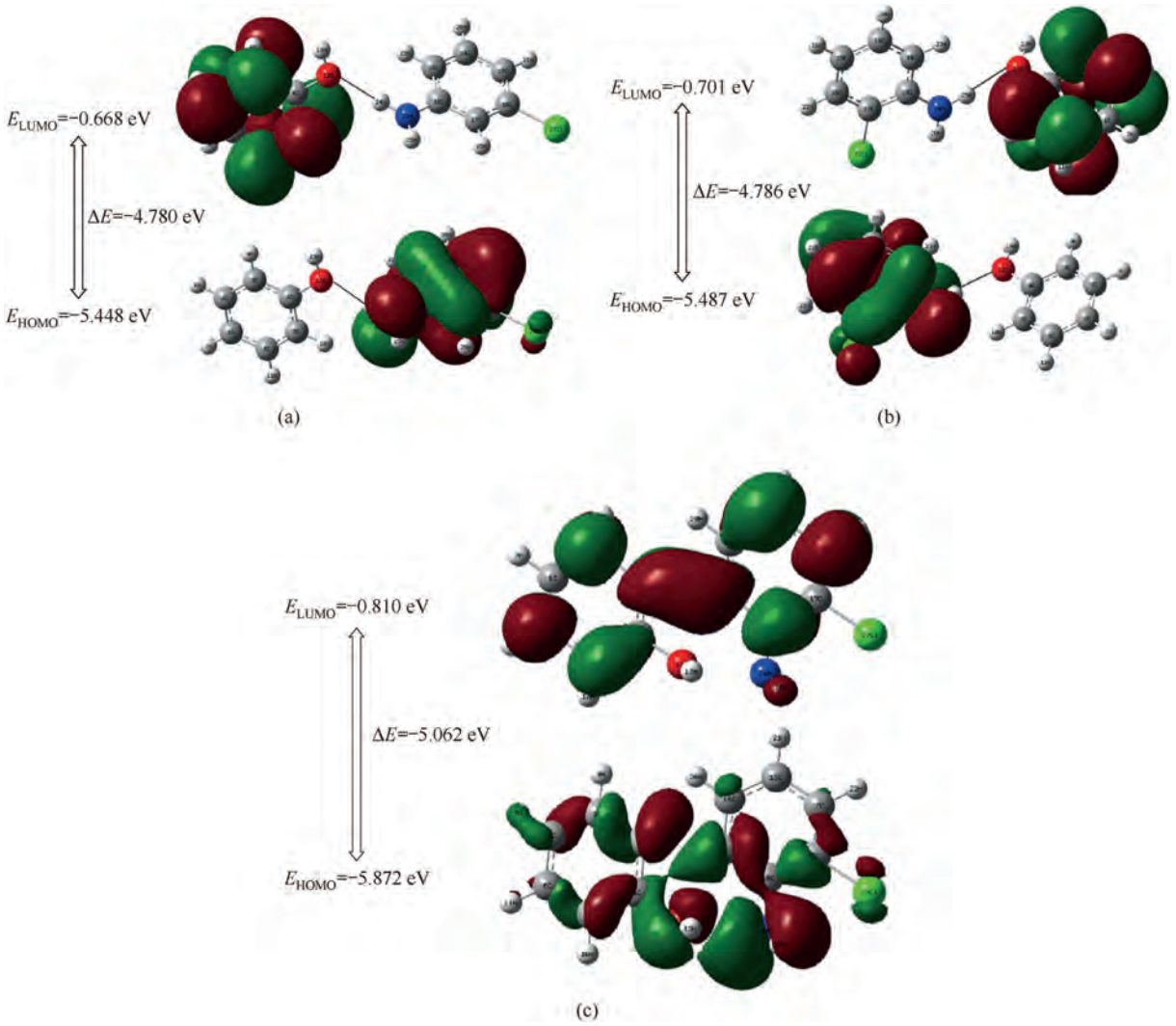

Fig. 8. Molecular representation of HOMO and LUMO of (a) cyclohexanol + *m*-CA, (b) cyclohexanol + *o*-CA and (c) cyclohexanol + aniline.

6. Conclusions

The results of the experiment show that distinct intermolecular interactions exist in each system, and the measured density and ultrasonic velocity values, as well as the assessed values of different thermodynamical parameters, are all included. $V_m^E, \kappa_S^E, L_f^E, Z^E$ and u^E the excess/deviation properties, outcome for every system fitting by the Redlich Kister polynomial equation. The presence of attractive contacts due to molecules belonging to a single element being accommodated within the interstitial position of another components of network structure is suggested by the negative deviation of V_m^E, κ_S^E and L_f^E. Additionally, it implies that in the interactions between the solvent and the solute in the aqueous solutions, the result is a significant packing phenomena. In addition, data on the molecular geometry, Ionization Potential, electrochemical stability, interaction energies, chemical reactivity descriptors, and numerous other molecular properties of the systems under study have been obtained by the DFT (B3LYP) 6-31 ++G (d,p) computations. Changes in the structural characteristics have been seen as a result of interactions within the molecular systems under study. The cyclohexanol + aniline solvent has demonstrated increased chemical reactivity in the cyclohexanol + aniline and chloro substituted aniline systems, according to HOMO-LUMO spatial plots.

CRediT Authorship Contribution Statement

E A Lohith: Methodology, Data curation, Conceptualization. S. Ravikumar: Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Formal analysis, Data curation, Conceptualization. K. Keerthi: Formal analysis, Data curation. S. Ponnusamy: Validation, Supervision, Software. Sada Venkateswarlu: Validation, Data curation. K. Siva Kumar: Writing – review & editing, Writing – original draft, Visualization, Conceptualization. N.V.V. Jyothi: Visualization, Validation, Methodology, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this work.

Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjche.2025.02.035.

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