

Volumetric, acoustical and computational study on molecular interactions in binary mixtures of Ricinoleic acid with some halobenzenes

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Densities (ρ) and speed of sound (u) of binary liquid mixtures of Ricinoleic acid with some halobenzenes at 303.15, 308.15 and 313.15 K and atmospheric pressure have been reported over the entire composition range. From the experimentally measured density (ρ), excess molar volumes (V_m^E), have been calculated. Deviation of the speeds of sound (Δu), isentropic compressibility (κ_s), deviation in isentropic compressibility ($\Delta\kappa_s$), deviation in acoustic impedance (ΔZ) and intermolecular free length (L_f) have been calculated using experimentally measured speed of sound, (u). Various theoretical speeds of sound and average deviations have been calculated using well established equations like Nomoto (U_{nmt}), Ideal Mixing Rule (U_{imr}), Junji (U_{junji}) and Jacobson's Free Length Theory, (U_{flt}). To derive fitting coefficients, (A_i) with standard deviation, (σ), excess properties have been fitted with the Redlich-Kister type polynomial equation. The variation of these properties with composition and temperature has been discussed in terms of molecular interaction on mixing and their interacting abilities. Observations reveal that there have been strong interactions between components. Strength of interactions between components has been described with theoretical computational calculations.

Keywords: Density, Speed of sound, Excess molar volume, Isentropic compressibility, Computational calculation, NBO analysis

Castor oil is pale-yellow thick oil and it is rich in Ricinoleic acid which has a powerful therapeutic effect. It is used as an excellent anti-oxidant and anti-inflammatory oil. Castor oil has been used for many years for the treatment of many skin infections and for healthy hair growth, it was used to preserve food due to its strong antimicrobial properties in earlier times. In India, it was a popular folk medicine that was used as a laxative and to improve memory. It plays an important role in Indian traditional medicine (Ayurvedic medicine) till date. Castor oil, as a component of less expensive vegetable oils can be used as feedstock in the production of biodiesel and this fuel can be use in cold winters¹.

Study of binary mixture of liquids in terms of theoretical models plays vital role to understand the type and relative strength of various weak or strong molecular interactions present in complex fluid state². Density measurements of binary liquid mixtures are essential for determination of composition of binary mixtures usually for non-ideal mixtures where direct experimental measurements are performed over the entire composition range².

Ricinoleic acid is major component of castor oil and there are a few methods available for its separation. Separation of Ricinoleic acid is a tedious and time consuming, which raises its cost, so new cost effective methods for separation of Ricinoleic acid from castor oil are required. Our group has been studying behavior of Ricinoleic acid in different group of solvents by providing electron donating or electron accepting environments to find its interaction with them.

Detailed literature review has revealed that no study has been carried out on the physico-chemical properties of Ricinoleic acid, the main component of castor oil. So, in the present paper, it was decided to study densities and speed of sound effect on binary mixtures of Ricinoleic acid with halo substituted benzenes.

Material and Methods

Chemicals

Ricinoleic acid (with >95% purity, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan), fluorobenzene (with 99% purity, S. D. Fine Chem. Ltd., India), chlorobenzene (with 99% purity, S. D. Fine Chem. Ltd., India), bromobenzene (with 99% purity, S. D. Fine

Chem. Ltd., India) were used in this study as received. List of chemicals with details like CAS number, molar mass, chemical formula, supplier, purity and comparison of experimental values of densities (ρ) in $\text{g}\cdot\text{cm}^3$ and speed of sound (u) in $\text{m}\cdot\text{s}^{-1}$ with literature values are reported in Table 1 and 2.

Apparatus and procedure

Binary mixtures were made by mixing of two liquids with different volumes by weighing in Reptech RA-2012 electronic balance to an accuracy ± 0.0001 g in specially designed ground glass air tight ampules. Preferential evaporation losses of solvent from the mixture were kept to minimum as evidenced by repeated measurements of physical properties over an interval of 2–3 days, during which time no changes in physical properties were observed. The uncertainty in the mole fraction of the mixtures was estimated to less than ± 0.0001 .

Densities and speeds of sound were measured by using automatic density and sound velocity meter (Anton Paar, DSA 5000 M, Anton Paar India Pvt. Ltd., Gurgaon, India). The instrument was calibrated

by using highly pure deionized water provided by manufacturer. Temperature compensation in the instrument is achieved with inbuilt integrated Pt 1000 temperature sensor having measuring scale $0\text{ }^\circ\text{C}$ to $70\text{ }^\circ\text{C}$ ($32\text{ }^\circ\text{F}$ to $158\text{ }^\circ\text{F}$) with accuracy of $0.001\text{ }^\circ\text{C}$ ($0.002\text{ }^\circ\text{F}$) during the measurement. The accuracy in measurement of densities and sound velocities were $\pm 0.000001\text{ g}\cdot\text{cm}^{-3}$ and $\pm 0.01\text{ m}\cdot\text{s}^{-1}$ respectively.

All computational calculations were carried out using Gaussian²⁰ 16 and all visualization of Gaussian calculations were carried out using Gauss View²¹ 6 software.

Calculations

Mathematical Representation of Excess or Deviation Functions

All the excess and deviation in properties have been fitting with the Redlich-Kister²² fourth order polynomial equation for representing excess or deviation functions for binary mixtures:

$$(Y)^E = x_1(1 - x_1) \sum_{i=1}^n A_i(2x_1 - 1)^i \quad \dots (1)$$

Where, Y^E = excess/ deviation properties, x_i represents mole fraction of i^{th} component, A_i is fitting

Table 1 — Experimental and Literature Values of Densities (ρ) of Pure Components at T = (303.15, 308.15 and 313.15) K

| | 303.15 K | | 308.15 K | | 313.15 K | |
|-----------------|--------------|---|--------------|---|--------------|---|
| | Experimental | Literature | Experimental | Literature | Experimental | Literature |
| Ricinoleic acid | 0.935521 | | 0.932138 | | 0.928738 | |
| Fluorobenzene | 1.013097 | 1.01316[3] 1.01314[4] [5] | 1.007057 | | 1.000977 | |
| Chlorobenzene | 1.095771 | 1.09547[6] 1.09500[9] | 1.090368 | 1.09006[6] 1.09000[9] 1.0820[17] 1.08960[12] | 1.084941 | 1.08366[8] 1.08200[7] |
| Bromobenzene | 1.481918 | 1.09510[11] 1.48148[6] 1.48147[8] 1.48100[9] | 1.475155 | 1.47481[6] 1.47300[9] | 1.468338 | 1.08480[13] 1.46700[7] 1.46708[10] 1.46800[14] |

Table 2 — Experimental and Literature Values of Speed of Sound (u) of Pure Components at T = (303.15, 308.15 and 313.15) K

| | 303.15 K | | 308.15 K | | 313.15 K | |
|-----------------|-----------------|---|--------------|----------------------|--------------|---------------------------------|
| | Experimental | Literature | Experimental | Literature | Experimental | Literature |
| Ricinoleic acid | 1468.20 | | 1451.81 | | 1435.70 | |
| Fluorobenzene | 1145.29 1145 | 1171[3] 1172[15] [16] | 1125.26 | | 1105.04 | |
| Chlorobenzene | 1249.33 | 1249[6] 1252[3] 1256[7] | 1231.22 | 1235[6] 1224[10] | 1212.98 | 1212[11] 1212[7] 1206[18] |
| Bromobenzene | 1138.27 | 1131[17] 1146[18] 1137[17] 1137[7] | 1122.88 | 1122[10] 1120[19] | 1107.62 | 1109[18] 1118[17] |

coefficient. The fourth-order form of equation of the Redlich-Kister equation gives the minimum standard deviation in Y^E . The standard deviation (σ) have been calculated using following relation:

$$\sigma(Y) = \left[\frac{\sum(Y_{exp}^E - Y_{cal}^E)}{N-P} \right]^{\frac{1}{2}} \quad \dots (2)$$

Where, Y_{exp}^E , Y_{cal}^E represent experimental and calculated values of excess properties, respectively. N is the number of experimental points and P is the number of parameters of the Redlich-Kister equation. The values of Fitting coefficients (A_0, A_1, A_2, A_3, A_4) with standard deviation (σ) in least square representation of V_m^E , Δu , Δk_s , Δz for studied binary mixtures were reported in Supplementary Data.

Molar Volume (V_m)

Molar volumes have been calculated from experimental measured density data. The following equation has been used to calculate molar volume for pure components and for mixtures respectively:

$$V_i (cm^3 mol^{-1}) = \frac{M_i}{\rho_i} \quad \dots (3)$$

$$V_m (cm^3 mol^{-1}) = \left(\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right) \quad \dots (4)$$

Where, x_i , M_i are the mole fraction, molar mass of i^{th} component, respectively. ρ_i and ρ_m are the density of i^{th} component and mixture, respectively.

Excess Molar Volume (V_m^E)

Excess molar volume (V_m^E) has been calculated using following standard equation:

$$V_m^E (cm^3 mol^{-1}) = V_m - V_1 x_1 - V_2 x_2 \quad \dots (5)$$

$$V_m^E (cm^3 mol^{-1}) = \left(\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right) - \left(\frac{x_1 M_1}{\rho_1} \right) - \left(\frac{x_2 M_2}{\rho_2} \right) \quad \dots (6)$$

Where, V_m , V_1 and V_2 , are the molar volumes of mixture and component 1 and 2, respectively.

Deviation in Speed of Sound (Δu)

Deviation in the speed of sound (Δu) has been calculated using the following relation:

$$\Delta u (m s^{-1}) = u_{exp} - (x_1 u_1 + x_2 u_2 + x_3 u_3 \dots) \quad \dots (7)$$

$$\Delta u (m s^{-1}) = u_{exp} - (x_1 u_1 + x_2 u_2) \quad \dots (8)$$

Where, u_{exp} represents speed of sound of mixture. x_1, x_2 and u_1, u_2 represents mole fraction and speed of sound of pure component 1 and 2, respectively.

Isentropic compressibility (k_s), Deviation in isentropic compressibility (Δk_s), Acoustical impedance (z), Deviation in Acoustical impedance (Δz) and Intermolecular free length (L_f)

These properties are calculated using following relations²³:

$$k_s (T Pa^{-1}) = \frac{1}{u_i^2 \rho_i} \quad \dots (9)$$

$$Z (g \cdot m^{-2} \cdot s^{-1}) = u_i \rho_i \quad \dots (10)$$

$$L_f = K k_s^{1/2} \quad \dots (11)$$

$$\Delta k_s = k_{s_{exp}} - (x_1 k_{s_1} + x_2 k_{s_2}) \quad \dots (12)$$

$$\Delta z = z_{exp} - (x_1 z_1 + x_2 z_2) \quad \dots (13)$$

Where, $x_1, x_2, \phi_1, \phi_2, k_{s_1}, k_{s_2}$ and z_1, z_2 represent mole fraction, volume fraction, isentropic compressibility and acoustical impedance of component 1 and 2 respectively. $k_{s_{exp}}$ and z_{exp} represents isentropic compressibility and acoustical impedance of binary mixtures. u_i and ρ_i represent speed of sound and density of i^{th} component respectively. K is the temperature dependent Jacobson constant.

From the isentropic compressibility following expression was derived to calculate the intermolecular free length (L_F):

$$L_F = K k_s^{1/2} \quad \dots (14)$$

Where, $K = [(93.875 + 0.375T) \times 10^{-8}]^4$ is temperature dependent Jacobson constant.

Theoretical Models of Speed of Sound

Following models are used in the present study to calculate theoretical speed of sound:

(i) Junjie Equation

Experimental values of speed of sound are generally compared with those obtained from the Junjie's equation²⁴, which has the following form

$$u_{junjie} = \frac{\left\{ \left(\frac{x_1 M_1}{\rho_1} \right) + \left(\frac{x_2 M_2}{\rho_2} \right) \right\}}{\left\{ (x_1 M_1 + x_2 M_2)^{\frac{1}{2}} \left[\left(\frac{x_1 M_1}{\rho_1 u_1^2} \right) + \left(\frac{x_2 M_2}{\rho_2 u_2^2} \right) \right]^{\frac{1}{2}} \right\}} \quad \dots (15)$$

Where, x_i, M_i, ρ_i and u_i are the mole fraction, molecular weight, density and speed of sound for component 1 and component 2 respectively.

(ii) Nomoto Equation

Theoretical values of speed of sound were also obtained using Nomoto equation²⁵

$$u_{nom} = \left\{ \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right\} \quad \dots (16)$$

Where, V_i is the molar volume of component 1 and component 2 and R_i is Wada's constant and is calculated as

$$R_i = u_i^{1/3} V_i \quad \dots (17)$$

Where, u_i is the speed of sound of i^{th} component.

(iii) Ideal mixture relation

Van deal and Van Geel²⁶ proposed the following expression for the estimation of sound velocity u_{imr} in an ideal mixture using sound velocities in the pure components

$$u_{imr} = \left[\frac{1}{(x_1 M_1 + x_2 M_2)^2} \right] \left\{ \frac{1}{\left[\left(\frac{x_1}{M_1 u_1^2} \right) + \left(\frac{x_2}{M_2 u_2^2} \right) \right]^{1/2}} \right\} \quad \dots (18)$$

Where M_1, M_2 and u_1, u_2 are the molar masses and sound velocities of first and second components, and u_{imr} is the ultrasonic velocity of ideal mixture.

(iv) Free Length Theory

According to Jacobson's theory²⁷ of free length, the ultrasonic velocity is given by

$$u = \frac{K}{L_f \rho^2} = \frac{KY}{2V_a \rho^2} \quad \dots (19)$$

For the Binary liquid mixture Eqn 19 becomes

$$u = \frac{K(x_1 Y_1 + x_2 Y_2)}{2[V_M - (x_1 V_{0,1} + x_2 V_{0,2})] \rho^2} \quad \dots (20)$$

Y is an adjustable parameter in the evaluation of velocity in liquid mixtures. Y can be obtained from velocity of pure liquids using Eqn 19:

$$Y = \frac{2V_a u \rho^2}{K} \quad \dots (21)$$

Where K is the temperature dependent Jacobson's constant²⁸, V_a is the available molar volume, which is the difference between the molar volumes at T (K) and 0 (K), is a direct measure of the compactness and the strength of bonding between the molecules of a liquid in mixture. V_a is given by the following equation:

$$V_a = V_M - V_0 \quad \dots (22)$$

When Y in Eqn 20 is replaced according to Eqn 21 and when the resulting expression obtained after rearrangement is as under:

$$u_{flt} = \frac{\left\{ \left[x_1 (V_{M1} - V_{0,1}) u_1 \rho_1^{1/2} \right] + \left[x_2 (V_{M2} - V_{0,2}) u_2 \rho_2^{1/2} \right] \right\}}{[V_M - (x_1 V_{0,1} + x_2 V_{0,2})] \rho^{1/2}} \quad \dots (23)$$

Eqn 21 says that according to the free length theory the square root of the inverse of the adiabatic compressibility of liquid mixture ($u\rho^{1/2}$) is the sum of the available volume fraction average of the square root of the inverse of adiabatic compressibilities of the individual components.

Theoretical computational calculations

Theoretical computational calculations such as geometrical optimization, vibrational calculation (IR), single point energy calculation, and NBO (Natural Bonding Orbitals) analysis were calculated using Hybrid function of DFT method, Beck's three parameters exchange functional B3 with the corrected correlation function of Lee-Yang-Par (LYP) with 6-31+G(d,p) and 6-31G(d,p) basis set. The complete conversation of finally optimized structures was confirmed by the absence of the imaginary frequency in vibrational calculation.

Results and Discussion

Densities, (ρ) and Excess molar volumes, (V_m^E)

The experimental values of densities, (ρ) and calculated excess molar volumes, (V_m^E) of Ricinoleic acid + fluorobenzene, + chlorobenzene, + bromobenzene mixtures at 303.15, 308.15 and 313.15 K are presented as a function of mole fraction of Ricinoleic acid (x_1) in Supplementary Data, Table S1. The values of fitting coefficients (A_0, A_1, A_2, A_3, A_4) of the Redlich-Kister polynomial equation are listed in Supplementary Data, Table S2. The graphical representation of (V_m^E) vs mole fraction (x_1) is given in Fig. 1.

V_m^E values are negative over the whole composition range at all three temperatures for all the three binary mixtures. The maxima occur between 0.54 to 0.58 mole fraction of Ricinoleic acid (x_1). The absolute values of V_m^E increases with rise in temperature. When mixtures change from fluorobenzene to bromobenzene, the negative values of V_m^E become less negative (i.e. increases). In general, the negative V_m^E values indicates for volume contraction on mixing and also means that the mixtures are more compressible than the corresponding ideal mixtures and it comes from specific intermolecular interactions²⁹. These interactions may be due to charge transfer and the structural contributions due to geometrical fitting of one component into another due to differences in molar volume of pure components³⁰. The negative

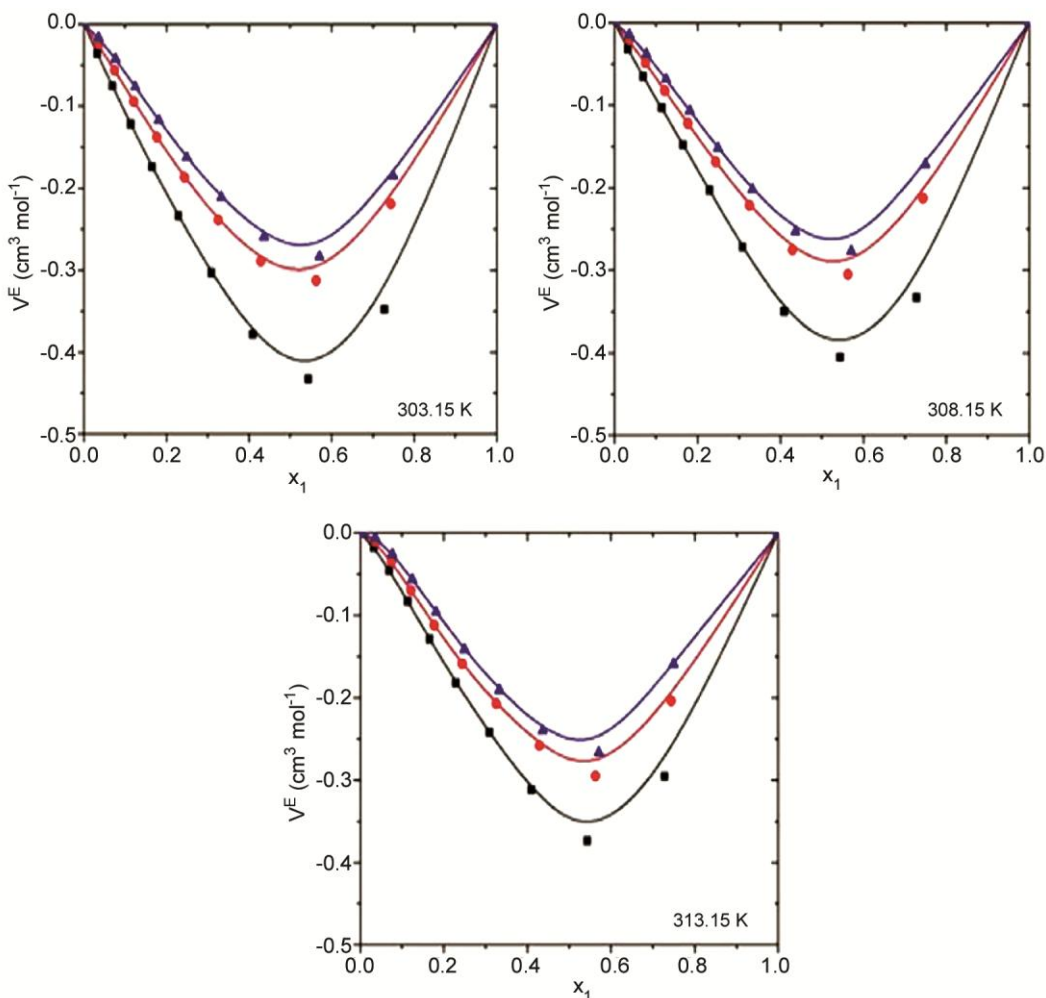


Fig. 1 — Excess Molar Volume (V^E) vs Mole Fraction (x_i) for Ricinoleic Acid + Fluorobenzene (■), + Chlorobenzene (●), + Bromobenzene (▲) at 303.15, 308.15 and 313.15 K

contributions also come from changes of free volume in the real mixtures due to physical, chemical, and structural characteristics of liquids³¹. In present case, negative V_m^E values indicate that there is a volume contraction on mixing which may result from physical and non-specific interactions between Ricinoleic acid and selected halobenzenes.

V_m^E values are negative and these values become less negative as the mixture changes from Ricinoleic acid + fluorobenzene to Ricinoleic acid + bromobenzene, suggesting that intermolecular interactions are strong in fluorobenzene binary mixture as compared to chloro- and bromobenzene binary mixtures. This may be due to fact that the size of the halo atom increases from fluorine to bromine atom and also decreases in electronegativity. The H-bond formation between the halo atom and hydrogen strongly depend on the electronegativity of the halo atoms^{32,33}.

The order of interaction of Ricinoleic acid with halobenzenes is as under:

Fluorobenzene > Chlorobenzene > Bromobenzene

Speed of Sound (u) and Deviation in Speed of Sound (Δu)

Deviation in the speed of sound, (Δu) are calculated from the experimentally measured speed of sound, (u) over the whole composition range and at all studied temperatures. The values of u and (Δu) are given in Supplementary Data, Table S3. The graphical variation of Δu values as function of mole fraction, (x_1) of Ricinoleic acid is shown in Fig. 2 at 303.15, 308.15 and 313.15 K. The values of fitting coefficients (A_0, A_1, A_2, A_3, A_4) of the Redlich-Kister polynomial equation are listed in Supplementary Data, Table S4. Δu values are positive for all these mixtures and maxima of the curve lies between 0.40 to 0.44 mole fraction region. Highest Δu values are obtained

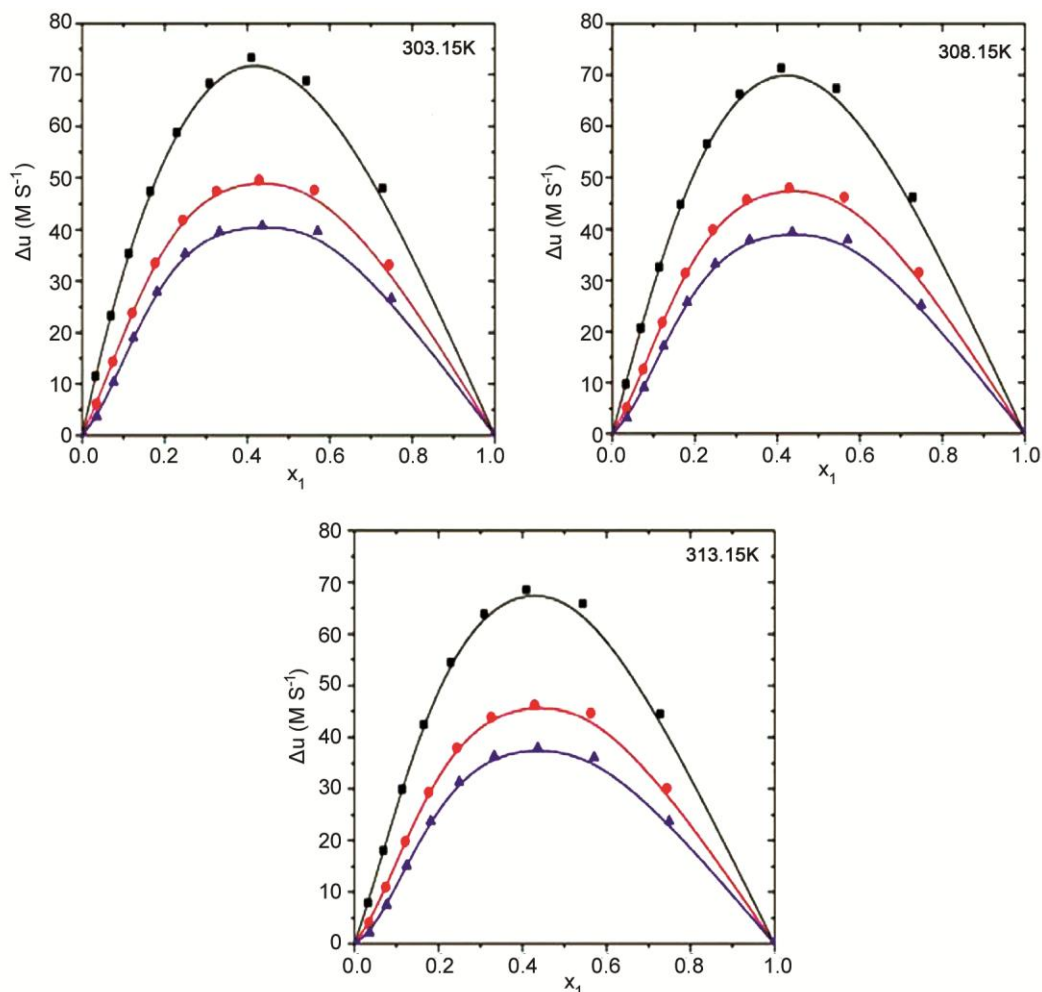


Fig. 2 — Deviation in Speed of Sound (Δu) vs Mole Fraction (x_i) for Ricinoleic Acid + Fluorobenzene (■), + Chlorobenzene (●), + Bromobenzene (▲) at 303.15, 308.15 and 313.15 K.

for Ricinoleic acid + fluorobenzene binary mixtures. With increase in temperature, Δu values systematically decrease³⁴.

The Δu values are large and change from positive to less positive values. It also indicates for strong interaction in Ricinoleic acid + Halobenzenes binary mixtures and the order is found fluorobenzene > chlorobenzene > bromobenzene, which is similar as observed for V_m^E values. In general, positive deviation in Δu values indicate the presence of strong interaction and negative deviation in Δu indicate the presence of weak interactions between the unlike molecules^{35,36}. The positive Δu values support that there is a strong interaction between Ricinoleic acid + fluorobenzene molecules. Due to close packing of molecules in the binary mixture, sound waves can easily pass through the molecules and deviation in speed of sound, (Δu) values become positive.

Theoretical relations of speed of sound

Various theoretical speed of sound relations such as Nomoto, (u_{nmt}), Ideal Mixing Rule, (u_{imr}), Junji, (u_{junjie}), and Jacobson's Free Length Theory, (u_{flt}) were calculated with their average deviation (σ). These values are listed in Supplementary Data, Table S10.

It can be observed from data that

- (i) Ideal mixture relation (u_{imr}) have highest values for Ricinoleic acid + fluorobenzene and + chlorobenzene binary mixtures. For fluorobenzene containing binary mixture, highest values are obtained for free length theory, (u_{flt}).
- (ii) Lowest σ values are obtained for u_{junjie} , u_{nmt} and u_{imr} for Ricinoleic acid + fluorobenzene, + chlorobenzene and + bromobenzene binary mixtures respectively at all studied temperatures.

Isentropic compressibility, (κ_s) Acoustical impedances, (z) and Intermolecular free length, (L_f)

Isentropic compressibility, (κ_s) acoustical impedances, (z) and intermolecular free length, (L_f) are calculated using the experimentally measured speed of sound, (u) and their values are listed in Supplementary Data, Table S5, S7 and S9 respectively. The parameters, A_i and standard deviation, σ are presented in Supplementary Data, Table S6 and Table S8.

Values of κ_s and L_f increase with increase in temperature for all three binary mixtures. The volume expansion of the mixture leads to increase in κ_s and L_f values with rise in temperature³⁷. The value of z decrease with increase in temperature which results due to less close packing of molecules with increase in temperature³⁸. In general, speed of sound and L_f has been reported to vary as the inverse of each other²⁹. Speed of sound increases steadily with increase in concentration of Ricinoleic acid and temperature; and L_f values decreases with increases of concentration of Ricinoleic acid.

The L_f values increases with rise in the temperatures from 303.15 to 313.15 K. As the temperature increases, there is loosening of intermolecular forces due to thermal agitation of molecules, this increases L_f values and this interaction become weaker at high temperatures³⁹.

Deviation in Isentropic Compressibility, ($\Delta\kappa_s$) and Deviation in Acoustical Impedance, (Δz)

The calculated values of deviation in isentropic compressibility, ($\Delta\kappa_s$) and deviation in acoustical impedance, (Δz) for all binary mixtures over the whole composition range are reported in Supplementary Data, Table S5 and S7 respectively. The graph of $\Delta\kappa_s$ and Δz vs x_1 of Ricinoleic acid are given in Fig. 3 and 4 respectively. The parameters, A_i and standard deviation, σ are presented in Supplementary Data, Table S6 and Table S8. The Δz values shift from positive to negative when second components changes from fluorobenzene to bromobenzene for all binary mixture at all studied temperatures.

Δz values are positive for Ricinoleic acid + fluorobenzene and negative for Ricinoleic acid + bromobenzene while for chlorobenzene mixture Δz values are slightly positive and negative. Negative Δz values indicate for weak intermolecular interaction in binary mixture⁴⁰⁻⁴¹. Δz values also support the view

that interaction become weaker when binary mixture changes from fluorobenzene to bromobenzene. Negative $\Delta\kappa_s$ values indicate for strong interaction and positive $\Delta\kappa_s$ values indicate for weak interactions in binary mixtures⁴². $\Delta\kappa_s$ values are both positive and negative for fluorobenzene and chlorobenzene binary mixtures but only positive for bromobenzene binary mixtures. $\Delta\kappa_s$ values change from positive to more positive values, from negative to positive when binary mixture changes from fluorobenzene to bromobenzene. When there is a strong interaction, the molecules in binary mixture are close to each other and resultant isentropic compressibility, (κ_s) is less than its pure value. $\Delta\kappa_s$ values increase with rise of temperature^{43,44}.

It is well known that when two liquids having largely different properties are mixed, significant variation in the properties is found to either decrease or increase depending upon the properties of individual component⁴⁵. Here Ricinoleic acid having adiabatic compressibility 495.88 T. Pa⁻¹ is mixed with components having higher adiabatic compressibility of 752.52, 784.22 and 818.13 T.Pa⁻¹ for fluorobenzene, chlorobenzene, and bromobenzene respectively. The values of $\Delta\kappa_s$ are expected to change⁴⁶. Generally, the negative $\Delta\kappa_s$ indicates the presence of strong intermolecular interaction. But here, there is a vast difference in molecular size of mixing components, so $\Delta\kappa_s$ value are positive in present binaries.

The L_f values increase with rise in the temperature from 303.15 to 313.15 K. As the temperature increases, there is loosening of intermolecular forces due to thermal agitation of molecules that lead to increase in L_f values, so interaction become weaker at high temperatures⁴⁷.

Computational Calculations

Geometrical optimization, interaction energy, theoretical vibrational spectra and natural bonding orbital (NBO) analysis have been done using density functional theory (DFT) with hybrid method B3LYP. For an accurate description of calculation, the diffuse and polarization function augmented split valence type 6-31+G(d,p) basis set has been used because the polarity of molecule affects intermolecular hydrogen bonding. So, hydrogen bond orbitals need large space occupation⁴⁸.

The complete conversation to finally optimized structures was confirmed by the absence of the imaginary frequency in vibrational calculation. The

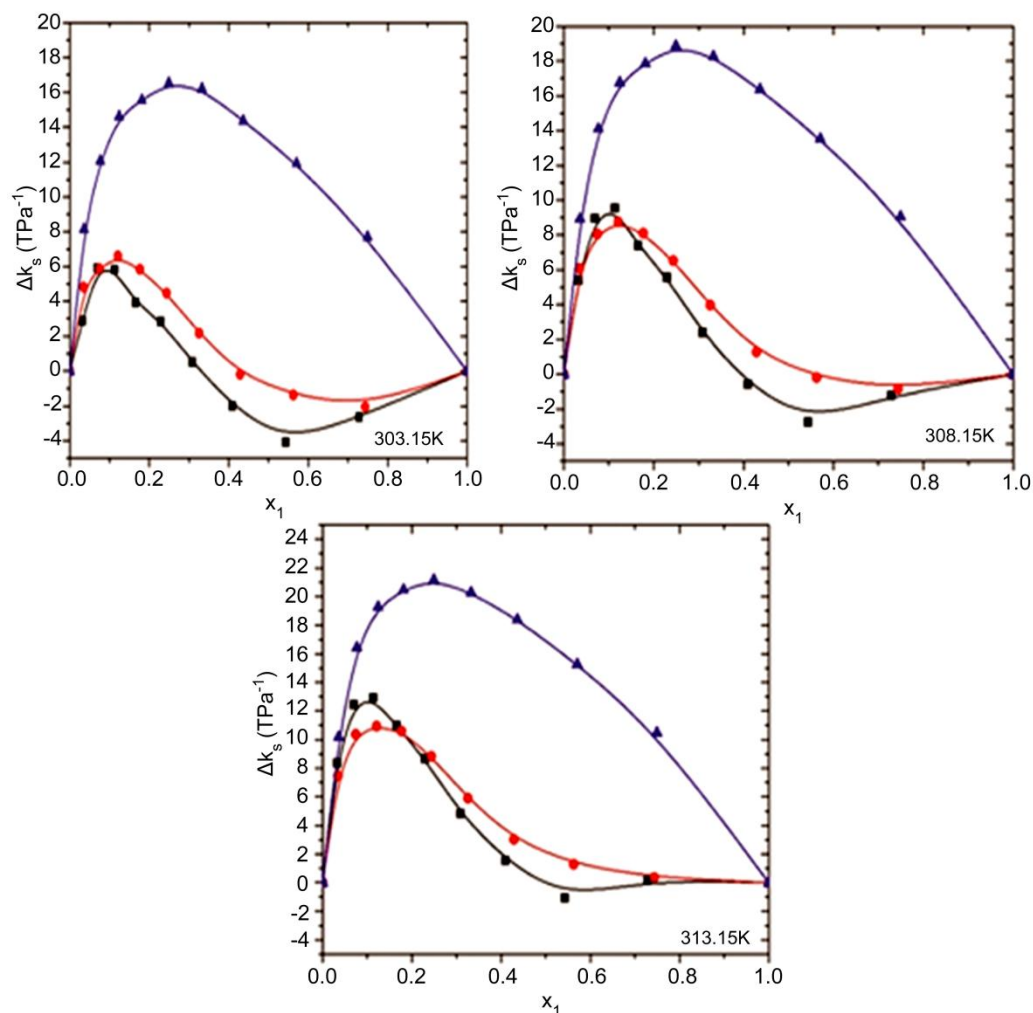


Fig. 3 — Deviation in Isentropic Compressibility (Δk_s) vs Mole Fraction (x_i) for Ricinoleic Acid + Fluorobenzene (■), + Chlorobenzene (●), + Bromobenzene (▲) at 303.15, 308.15 and 313.15 K.

values of bond length, Mulliken charges and bond angle between atoms of pure Ricinoleic acid, halobenzenes and their binary mixtures at 303.15 K are listed in Supplementary Data, Table S11, S12, S13 respectively. The optimized structures of pure components and their binary mixtures with Mulliken charge and 3D-MESP solvation state of Ricinoleic acid with halobenzenes (fluorobenzene, chlorobenzene and bromobenzene) are shown in Fig. 5 and in Supplementary Data, Fig. S1 and S2.

The oxygen atom of Ricinoleic acid possesses higher negative electrostatic potential -0.504522 , -0.424355 , -0.457758 Mulliken charge value and the H-atoms of Ricinoleic acid possesses higher positive electrostatic potential with to 0.326656 , 0.342823 Mulliken charge value, observed from Fig. 6 and from Supplementary Data, Fig. S3 and S4.

Similarly, for halobenzenes (fluorobenzene, chlorobenzene and bromobenzene), halogen atoms possess higher negative electrostatic potential -0.349115 , 0.171288 , -0.068554 and H-atom possess higher positive electrostatic potential 0.143299 , 0.144467 , 0.141600 . Considering these values, there may be following types of possible orientation of molecule which shows intermolecular interactions like forming of new H-bond and noncovalent interactions like dipole-dipole, dipole-induced dipole etc.

From NBO analysis Mulliken charges calculated for optimized structure show that Ricinoleic acid has $-\text{COOH}$, $-\text{OH}$, and $-\text{CH}_3$ groups and values of Mulliken charges for them are given in Supplementary Data, Table S12. Oxygen of $-\text{OH}$ group has -0.504522 , COOH group has -0.424355 ,

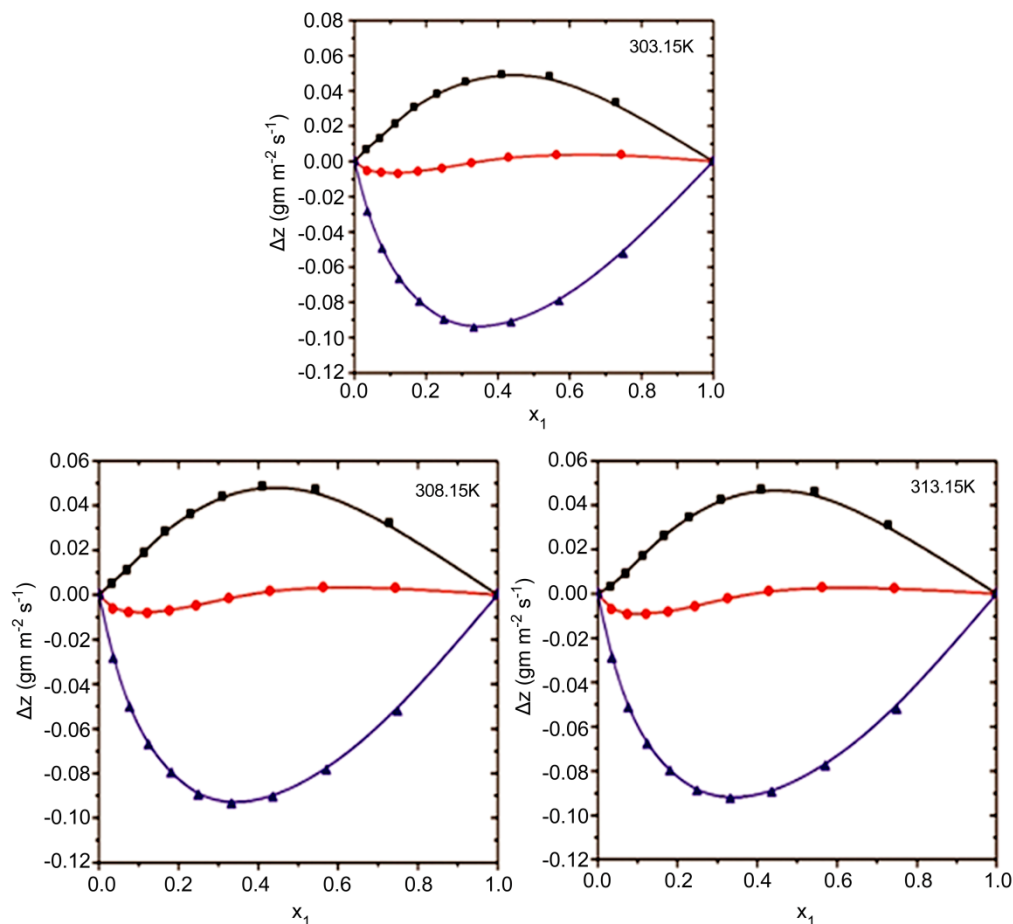


Fig. 4 — Deviation in Acoustical impedances (Δz) vs Mole Fraction (x_i) for Ricinoleic Acid + Fluorobenzene (■), + Chlorobenzene (●), + Bromobenzene (▲) at 303.15, 308.15 and 313.15 K.

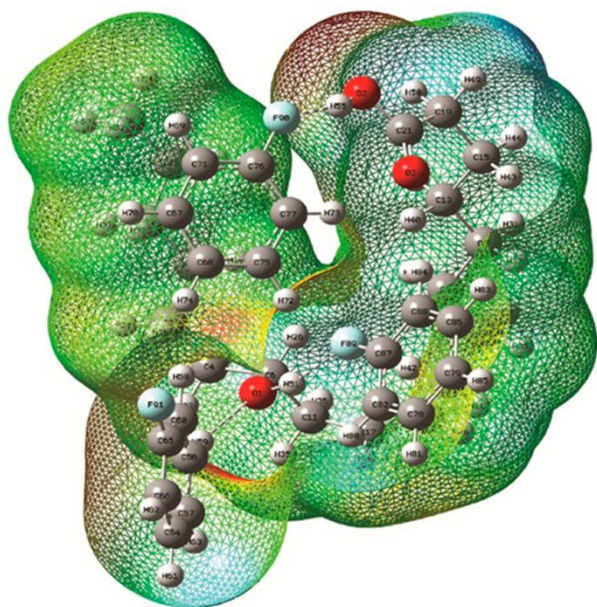


Fig. 5 — Optimized geometric structures of Ricinoleic Acid + Fluorobenzene binary mixture (with three interaction sites) in 3D MESP Surface based on B3LYP/6-31+G(d,p) at 303.15 K.

−0.457758 Mulliken charge values respectively. Hydrogen H55 attached with Carbon C19 has 0.362265 value. In Methyl group (−CH₃) has first hydrogen H52 with 0.144909, second hydrogen H53 with 0.144694 value and third hydrogen H54 with 0.142251 Mulliken charges. In general aliphatic hydrogens have higher positive charge than hydrogen atoms attached with ring.

In halobenzene, the halogen atom has some excess negative charge. In fluorobenzene, F12 has Mulliken charge as −0.349115, Chlorine with Cl12 (0.171288) and bromine with Br12 (−0.068554). Carbon and hydrogen has positive or negative charges which are shown in Supplementary Data, Table S12.

The hydrogen atoms attached with carbon atoms of aromatic ring possess some positive charge. So, there are chances of dipole-dipole or dipole-induced dipole or H-bonding between electropositive atom and lone pair containing electronegative atoms of Ricinoleic acid or halobenzene. Three possible interactions sites selected on the basis of theoretical data are given as under

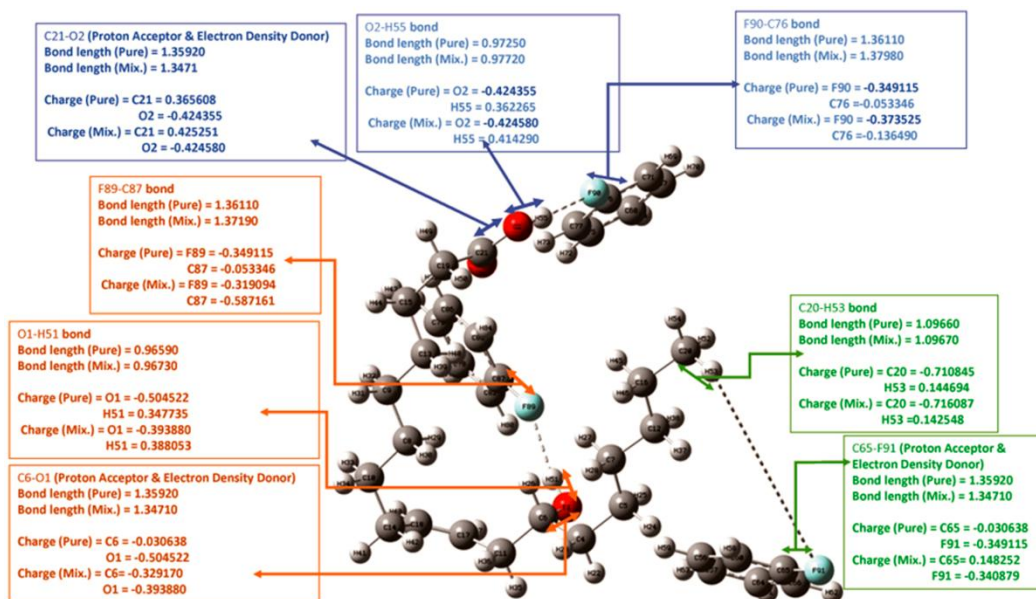


Fig. 6 — Bond length and Mulliken charges between atoms of pure Ricinoleic acid, Fluorobenzene and their binary mixtures at 303.15 K.

1. First possible interaction site

Interaction between positive charged H51 which attached with oxygen O1 atoms of –OH group of Ricinoleic acid and electronegative halogen (X) atom of halobenzene (F89, Cl89, Br89).

2. Second possible interaction site

Interaction between positive charged H55 which is attached with oxygen O2 atoms of –COOH group of Ricinoleic acid and electronegative halogen (X) atom of halobenzene (F90, Cl90, Br90).

3. Third possible interaction site

Interaction between positive charged H52 or H53 or H54 attached with C20 carbon atom of –CH₃ group of Ricinoleic acid and electronegative halogen (X) atom of halobenzene (F91, Cl91, Br91).

NBO Analysis

Natural bond orbital analysis is a very useful tool to investigate the charge transfer or conjugative interaction in binary molecular system. It also plays a vital role to study intra- and intermolecular bonding and interaction among bonds³³. Some electron donor orbitals, electron acceptor orbitals and interaction stabilization energy obtained from second order perturbation theory are reported in Supplementary Data, Table S14. The larger value of E(2) indicates more intensive interaction between electron donors to electron acceptors and the greater extent of conjugation in the whole system. Delocalization of electron density between occupied Lewis type NBO

orbitals (bond or lone pair) with formally unoccupied non-Lewis NBO orbitals (antibond or Rydberg) leads to stabilization of donor- acceptor interaction⁴⁹. Some important associations with second order perturbation energy for Ricinoleic Acid to fluorobenzene are listed as under.

1. First possible interaction site

- I. Interaction between F89 lone pair (1) \rightarrow $\sigma^*(\text{O1-H51})$ with 1.49 kcal mol⁻¹ energy value.
- II. Interaction between F89 lone pair (2) \rightarrow $\sigma^*(\text{O1-H51})$ with 2.19 kcal mol⁻¹ energy value.
- III. Interaction between O1 lone pair (1) \rightarrow $\sigma^*(\text{C56-H59})$ with 2.50 kcal mol⁻¹ energy value.

2. Second possible interaction site

- I. Interaction between F90 lone pair (1) \rightarrow $\sigma^*(\text{O2-H55})$ with 1.76 kcal mol⁻¹ energy value.
- II. Interaction between F90 lone pair (2) \rightarrow $\sigma^*(\text{O2-H55})$ with 5.56 kcal mol⁻¹ energy value.
- III. Interaction between F90 lone pair (3) \rightarrow $\sigma^*(\text{O2-H55})$ with 1.65 kcal mol⁻¹ energy value.
- IV. Interaction between O3 lone pair (1) \rightarrow $\sigma^*(\text{H73-C77})$ with 0.71 kcal mol⁻¹ energy value.
- V. Interaction between O3 lone pair (2) \rightarrow $\sigma^*(\text{H73-C77})$ with 0.94 kcal mol⁻¹ energy value.
- VI. Interaction between $\sigma(\text{O2-H55}) \rightarrow \sigma^*(\text{C76-F90})$ with 0.10 kcal mol⁻¹ energy value.

3. Third possible interaction site

- I. Interaction between $\sigma(\text{C56-H59}) \rightarrow \sigma^*(\text{O1-C6})$ with 0.10 kcal mol⁻¹ energy value.

II. Interaction between O1 lone pair (1) $\rightarrow \sigma^*(C56-H59)$ with $2.29 \text{ kcal mol}^{-1}$ energy value.

Similarly by important associations with second order perturbation energy between Ricinoleic acid and chlorobenzene or bromobenzene are listed in Supplementary Data, Table S14 and are shown in Supplementary Data, Fig. S3 and S4 respectively.

NBO analysis results support the presence of intermolecular interaction via hydrogen bonding in these selected binary mixtures.

Conclusions

The density, (ρ), and excess molar volumes, (V_m^E), of Ricinoleic acid with halobenzenes (fluorobenzene, chlorobenzene and bromobenzene) are reported at temperatures 303.15, 308.15 K and 313.15 K. Negative deviations are observed in V_m^E values for all binary mixtures indicate for presence of strong interaction in binary mixtures. The positive values of Δu , negative values of $\Delta \kappa_s$, and Δz suggest for strong interaction present between the molecules of binary mixtures. The order of interaction is fluorobenzene > chlorobenzene > bromobenzene in selected mixture. Results from theoretical relations of speed of sound are found in good agreement with experimental values. From the results, it is anticipated that there is possibility of hydrogen bonding type of interaction between the Ricinoleic acid and halobenzene molecules. These interactions become weaker when binary mixture change from fluorobenzene to bromobenzene and temperature changes from 303.15 to 313.15 K.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_58A\(11\)1194-1205_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_58A(11)1194-1205_SupplData.pdf).

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