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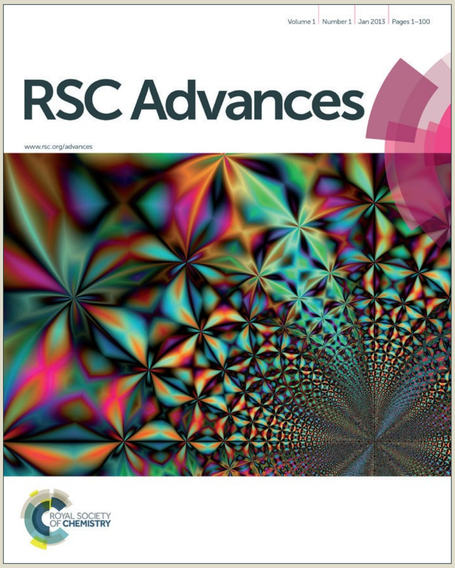

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Elucidation of hydrogen bonding formation by computational,FT-IR Spectroscopic and theoretical study between benzylalcohol with isomeric cresols

M.Raveendra[1], M.Chandrasekhar[2], C.Narasimharao[3], L.Venkatramanna[#4], K. Siva Kumar[*5], K. Dayananda Reddy[1]

[1]Department of Chemistry, P.V.K.N. Govt. Degree & P.G. College, Chittoor-517001, A.P., India.

[2]Department of Physics, Vignan Institute of Technology and Science, Deshmukhi, Telagana, India

[3]Department of Chemistry, S.V. University, Tirupati-517502, A.P., India.

[4]Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India.

[5]Department of Chemistry, S.V.Arts Degree & P.G.College (T.T.D'S), Tirupati-517502, A.P., India.

Abstract

The densities (ρ) of binary mixtures of benzylalcohol with *o*-cresol, *m*-cresol, *p*-cresol have been measured at ambient atmospheric pressure over the entire composition range and at temperature range from 303.15 K to 323.15 K with the help of Rudolph Research Analytical digital densitometer (DDH-2911 model). Moreover, the speeds of sound (u) for these mixtures were also carried out at 303.15 K and 313.15 K. The measured data were used to calculate the excess volumes (V^E) and excess isentropic compressibilities (κ_S^E) and the results were computed in terms of Redlich-Kister & Hwang equations. The experimental speed of sound was compared in terms of Schaff's collision factor theory (CFT) and Jacobson's free length theory (FLT).The experimental excess molar volume (V^E) also used to test validity of Prigogine-Flory-Patterson (PFP) theory at 303.15K and 313.15K. The existence of the hydrogen bonding in the binary mixtures of benzylalcohol with cresols are further conformed by high level theoretical calculation namely, the density functional theory (DFT-B3LYP) of 6-311++G (d, p) basis sets was used to study the geometries, bond characteristics, interaction energies and natural bonding orbital (NBO) analysis of the hydrogen bonded complexes in gas phase and the self, cross-associations in the mixture studied were investigated via quantum chemical calculations.. The measured data were used to study intermolecular interactions between component molecules of binary mixtures with FT-IR Spectroscopic studies.

Keywords: Binary mixture; Excess properties; DFT; Interaction energy; NBO; FT-IR.

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*Corresponding Author

E-mail: sivakumarkasi64@gmail.com, Mobile: +91-9290080843

Former Research associate

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1. Introduction

Thermo physical properties of mixtures which contain blend of organic solvents with cresols are important from technological and theoretical points of view [1, 2]. In terms of practical applications these thermodynamic properties are essential for elaborate estimation of varying thermodynamic models required in optimized processes of the chemical, petrochemical, pharmaceutical and other industries

The liquids that were chosen in the present investigation have many potential uses towards chemical industries. Benzylalcohol is used as versatile solvent for shellac, gelatin, cellulose acetate and for pharmaceutical aid as an antimicrobial agent [3-5], in the manufacture of perfuming substances, as an embedding materialin microscope and in veterinary medicines [6]. Cresols are one of the most important groups of aromatic organic compounds, used as disinfectants, organic intermediates, textile scouring agents, herbicides, surfactants and in the production of few phenolic resins, tri crysyl phosphate, salicylaldehyde, coumarin etc. Moreover, cresols are also utilized in the preparation of most widely applied substances namely Lysol and Creosote and as an end product in azo dyes. Thermodynamic properties of liquid mixtures containing cresols with different organic solvents were reported [7, 8].

The present investigation involving mixtures of benzylalcohol with isomeric cresols makes possible the study self-association via inter and intra molecular hydrogen bonds. In the present investigation, an attempt have been made to provide an insight in to the nature of molecular interactions occurring between benzylalcohol and cresols by measuring the densities (ρ) at 303.15 K to 323.15 K and speeds of sound (u) at 303.15 K and 313.15 K. Further, the change in position of -OH group in cresol molecule may modify both the sign and magnitude of excess thermodynamic functions. Moreover, the measured speed of sound data is also analyzed in terms of Schaff's collision factor theory (CFT) [9], Jacobson's free length theory (FLT) [10-12]. In this work we will analyze the excess molar volume with PFP theory. The present work was understand to determine the effect of addition of –OH group in toluene molecule and changing its position in *ortho, meta* and *para* positions may influence both the sign and magnitude of excess thermodynamic functions for the above said binary systems. Moreover, the characterization of intermolecular interactions at the molecular level was done through a quantum chemical approach [13], using density functional theory (DFT) method. This approach allowed a detailed picture of the Hydrogen bonding in the studied liquid mixtures and its relationship with macroscopic physico chemical properties to be obtained, providing information about the role of the involved functional groups of the liquid structuring. FT-IR Spectroscopic data is also collected in the

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present investigation to know the occurrence of intermolecular hydrogen bond between benzylalcohol and isomeric cresol molecules.

2. Experimental and Computational Methods:

2.1. Materials

The chemicals that were used in the present work are A.R. grade, supplied by S.D. Fine Chemical. Ltd., India. The before experimental measurements, all the liquids were purified as fractionally distilled as described elsewhere in the literature [14] and dried over 0.4nm molecular sieves. The mass fraction purities are analyzed by gas chromatography and the water content of solvents used in this work was measured by Analab (Micro Aqua Cal 100) Karl Fischer Titrator are given in Table 1. Moreover, the purity of chemicals was checked by comparing the measured densities and speed of sound with literature values at T=303.15Kto 323.15K, which are in good agreement and these were reported in Table 2.

2.2. Measurements

In the present work, benzylalcohol and cresol mixtures are prepared by weighing an appropriate amount of pure liquids an electronic balance (Afoset, ER –120A, India) with a precision of ± 0.1 mg by syringing each component into airtight stopper bottles to minimize the evaporation and moisture content. The uncertainty in the estimation of mole fraction was $\pm 1\times10^{-4}$. After mixing the sample, the bubble free homogenous sample is transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model) and the collection of data were already described earlier [15]. The uncertainty of density measurement liquid mixtures is $\pm 2 \times 10^{-3}$g.cm^{-3} and uncertainty of temperature is ±0.01 K. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 M.Hz, is used to measure the speed of sound data of the binary liquid mixtures at 303.15 K and 313.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound is ± 0.3% and uncertainty of temperature is ±0.02 K. The details of its calibration, the experimental setup and measuring procedure have been described previously [16].

The working of the interferometer was tested by comparing the measured speed of sound of pure samples of benzylalcohol and isomeric cresols, which are in good agreement with literature values [17-30] at T=303.15K is reported in Table 2. FT-IR spectra have been measured by ALPHA FT-IR Spectrometer (Bruker) to study the existence of intermolecular hydrogen bonding between benzylalcohol and isomeric cresols.

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2.3. Computational Details:

The optimized geometry, harmonic vibrational wave numbers and bond characteristics of the pure and equimolar hydrogen bonded complexes, interaction energy and natural bonding orbital (NBO) analysis have been calculated theoretically from density functional theory (DFT-B3LYP) [31-33] methods with 6-31 + G and 6-311 + G basis sets. All the calculations have been carried out using the Gaussian 09 computational package [34].

3. Results and discussion

3.1. Excess volumes (V^E)

The excess molar volumes (V^E) of binary mixtures benzylalcohol with isomeric cresols were calculated from the experimentally determined density data using the following equation:

$$V^E/cm^3.mol^{-1} = [[X_1 M_1 + X_2 M_2]/\rho_m - [X_1 M_1/\rho_1 + X_2 M_2/\rho_2]] \qquad (1)$$

where, X_1,X_2,M_1,M_2,$\rho_1$and$\rho_2$are the mole fraction ,molar weight and the density of pure component 1 and 2, respectively and ρ_m is the measured density of the mixture and the data were given in Table 3. Further, the V^E data were also graphically mentioned in Figures 1, 2 at 303.15K and 313.15K. The excess or deviation values of the interactions between the mixing species mainly depend upon the composition, the different alignment of size and shape of the component molecules.

The sign of excess volume of a binary system may be influenced by the relative strength of expansion and contraction of mixing of two component molecules. If the factors responsible for expansion dominate the factors contributing contraction, V^E becomes positive. On the other hand, if the contractive factors out way the expansion factors, then V^E becomes negative. The features that create expansion in volume are:

(a) The rupture of hydrogen bonding with one component by the other, or breakdown of self-association between component molecule held by weak forces like dipole-dipole or dipole-induced dipole interaction or by weak van der Waals forces.
(b) The geometry of component liquid structure which does not allow the fitting of the molecule in the moieties of each other.
(c) Steric hindrance which resists the closeness of the constituent component liquid species.

While the factors which contribute to contraction in volume are:

(a) Chemical interaction between molecules like hetero molecular association by the formation of hydrogen bonds leading to strong specific interaction.

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(b) Interstitial accommodation of molecules of one component into the cavities of the structural arrangement of molecules of the other component.

(c) The geometry of the liquid molecular structure which allow the fitting of one liquid molecule with each other.

An examination of V^E data in the Figures 1 and 2 reveal that, the property is negative at all temperatures over the entire composition range for the binary mixtures of benzylalcohol with *o*-cresol, *m*-cresol indicating that contraction in volume factors are dominant. On the other hand, contraction and expansion in volume factors are competing with each other in the binary mixture containing *p*-cresol. The intensity of molecular interaction between benzylalcohol with isomeric cresols follows the following order:

(benzylalcohol + *o*-cresol) > (benzylalcohol +*m*-cresol) > (benzylalcohol +*p*-cresol)

The strength of molecular interactions in an aromatic hydrocarbon was influenced by the nature of group which is present on benzene ring, which affects the sign and magnitude of excess thermodynamic functions. The overall electron density of the benzene ring may force hetero molecular interaction between component molecules. If two different or similar substituents are present on benzene ring, their relative orientation may also affect intermolecular interactions. If the separation between two substituents increases, the intermolecular interactions were also decreases [35, 36]. A comparison of chemical reactivity between *ortho, meta* and *para* isomers, the intermolecular interaction in *ortho* isomer cause a large excessive exertion in the ring and thereby making an opposite pole towards *ortho* side of the ring and thus giving a dipolar character. This causes the stronger interactions in *ortho* derivatives than the other two isomers. Hence, more negative V^E data was observed in *o*-cresol when compared to *m*-cresol. In the case of *p*-cresol the -OH group is situated at 4th position on benzene ring, offers maximum steric hindrance to benzylalcohol molecule and thus the overall electron donor-acceptor interactions in it are lower than *o*-cresol. Hence, it can be concluded that introduction of –OH group in *o, m, p*-positions of benzene molecule is influencing overall sign and magnitude of V^E data of all the binary liquid mixtures.

The more negative excess volume of the system benzylalcohol and *o*-cresol reveals that more efficient packing and/or dipole-dipole intermolecular interactions occurred between these two components when mixed together. Moreover, the V^E may be ascribed as the formation of hydrogen bond between the oxygen atom of the hydroxyl group of benzylalcohol and the hydrogen atom of the hydroxyl group of *o, m, p*-cresol molecules. In general, the departure of negative deviations from ideality in these binary liquid systems were attributed due to the

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interstitial accommodation and strong intermolecular interactions such as chemical or specific interaction of the molecules like hydrogen bonding, dipole–dipole interaction between the unlike molecules [37].

The more negative V^E data in the *o*-cresol system when compared to the other two isomers may be ascribed due to the closeness of –CH3 group to – OH group leads to an increase of electron density in the O-H bond and steric effect. These two effects increase the strength of intermolecular hydrogen bond formation in *o*-cresol than in *m*- and *p*- cresols. An examination of V^E data in Figures 1, 2 suggest that addition of –OH group in Toluene molecule is considerably influencing the sign and magnitude of V^E.

3.2. Excess isentropic compressibilities (κ_s^E):

Mole fraction (x_i), the experimental speed of sound (u)and calculated speed of sound data from theoretical models (FLT, CFT),isentropic compressibility's (κ_S) and excess isentropic compressibility (κ_s^E)data in terms of Redlich-Kister and Hwang et al. equation (2) and (3) respectively for the binary mixtures of benzylalcohol with *o*-cresol, *m*-cresol and *p*-cresol at 303.15K and 313.15K were included in Table 4. Further, the κ_s^E data of all the binary liquid mixtures were graphically depicted in Figures 3&4 at 303.15 K and 313.15K respectively.

The experimental density (ρ) and speed of sound (u) data used to compute the isentropic compressibility (κ_S) as [38]

$$\kappa_S = u^{-2}\rho^{-1} \tag{2}$$

The corresponding excess isentropic compressibilities (κ_s^E) were calculated employing the following equation [39]

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

where κ_s^{id} is the ideal value of the isentropic compressibility and was calculated from the following equation. The κ_s^{id} was given by an expression recommended by Benson and Kiyohara [39].

$$\kappa_{\mathrm{s}}^{\mathrm{id}} = \sum_{\mathrm{i=1}}^{2} \phi_{\mathrm{i}} \left[\kappa_{\mathrm{s.i}} + TV_{\mathrm{i}}\left(\alpha_{\mathrm{i}}^{2}\right) / C_{\mathrm{p.i}}\right] - \left\{ T\left(\sum_{\mathrm{i=1}}^{2} x_{\mathrm{i}} V_{\mathrm{i}}\right)\left(\sum_{\mathrm{i=1}}^{2} \phi_{\mathrm{i}}\alpha_{\mathrm{i}}\right)^{2} / \sum_{\mathrm{i=1}}^{2} x_{\mathrm{i}} C_{\mathrm{p.i}} \right\} \tag{4}$$

here, C_{pi} and α_i are the molar heat capacity and the thermal expansion coefficient of the i^{th} component respectively. The value of C_{pi} and α_i were obtained and evaluated from literature [3, 40-42].

An examination of κ_s^E data in Figures 3 and 4 reveals that the property is positive for the binary system containing benzylalcohol with *o*-cresol and the data is negative in

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the remaining systems. In general, the values of κ_s^E can be considered as arising from two types of interaction between the component molecules:

(i) The dispersion forces are interactions of the type namely weak dipole-dipole and destruction of molecular association present in the pure component liquid causing to positive κ_s^E data.

(ii) while geometric fitting of component molecules of two different sizes into each other's cavity and specific interaction like the formation of new hydrogen bond (-O...H-O-)resulting in negative κ_s^E values.

A study of curves in Figures 3 and 4 reveals that κ_s^E data is positive in the binary mixture of benzylalcohol with *o*-cresol indicate that physical parameters are dominant while structural factors are prevailing in the remaining mixtures. Moreover, negative κ_s^E values is an indication of the liquid mixtures is less compressible than the pure liquids, indicating that the molecules in the mixture are more effectively bind than in pure liquids. The observed positive κ_s^E values suggest that the breaking of liquid order due to the self-association of both benzylalcohol and *o*-cresol. Moreover, the negative κ_s^E value for the studied binary mixtures indicates that difference in molecular sizes and interstitial accommodation between the two mixture components (benzylalcohol + *m, p*-cresols). The negative values of κ_s^E were also an indication that the mixture is less compressible when compared to ideal mixture and indicate the existence of strong chemical and specific interactions between the components of analyzed binary mixtures. The values of κ_s^E become more negative as the strength of interaction between component molecules increases [43], due to dissociation of associated structure between benzylalcohol and *p*-cresol mixture forms strong O…H bond. The molecular structure of binary mixtures containing cresols and protic solvent like benzylalcohol, we can suggest that the addition of pure benzylalcohol to cresols would disrupt their self-associated structures their by releasing free benzylalcohol, *o*-cresol, *m*-cresol and *p*-cresol molecules may mix through by specific interactions and intermolecular hydrogen bonds forming the mixed intermolecular complexes.

Experimental speed of sound were analyzed in terms of collision factor theory (CFT)[9] and free length theory (FLT)[10, 11] these were also included in Table 4 along with experimental speed of sound. A comparison between experimental sound speed and theoretical values suggest that the model proposed by Schaaff's CFT gives better estimation of sound speed data. The merits of these theories were compared in terms of relative root mean deviation (RMSD) and mean percentage deviation (MPD) by using the following formulae.

$$RMSD = \left[\frac{1}{n}\sum_{i=1}^{n}\left[\frac{y_{exp}-y_{cal}}{y_{exp}}\right]^2\right]^{1/2} \qquad (5)$$

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$$MPD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{(y_i^{cal}-y_i^{exp})}{y_i^{exp}}\right| \quad (6)$$

The RMSD & MPD for all the binary system values are given in Table 5 shows that Schaaff's CFT model gives better estimation in speed of the sound for the binary mixtures under the investigation.

The experimental excess volume (V^E) and $\kappa_s{}^E$ values were compared in terms of Redlich-Kister [44] and Hwang *et al* [45] equations and these were also included in Table 4. The methods and calculation of V^E in terms of Redlich-Kister and Hwang equation were described earlier [46, 15]. The empirical relation proposed by Redlich-Kister is as follows:

$$V^E/cm^3.mol^{-1} = X_1(1-X_1)[a_0+a_1(2X_1-1)+a_2(2X_1-1)^2] \quad (7)$$

Hwang et al .equation is of the form:

$$V^E/cm^3.mol^{-1} = X_1X_2[b_0 + b_1X_1^3+b_2X_2^3] \quad (8)$$

where a_0 ,a_1, $a_2$and b_0,$b_1$and b_2 are adjustable parameters of Redlich-Kister & Hwang et al .equations and X_i is the mole fraction of component *i* (*i* = 1, 2) in the mixture. The values of parameters were obtained by the least-square method and these values of the parameters were given in Table S1.

The corresponding standard deviation σ (Y^E) for both Redlich-Kister and Hwang *et al* equations were also computed using the relation and are given in Tables S1 and S2 calculated by applying the following formula

$$\sigma(Y^E) = [\Sigma(Y^E_{exp} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (9)$$

where σ (Y^E) is V^E/κ_S^E.'m' is the total number of experimental points and 'n' is the number of coefficients . An examination of $\sigma(Y^E)$values in Tables S1 and S2 suggest that Redlich-Kister & Hwang equation give good estimation both in V^E and $\kappa_s{}^E$ of liquid mixtures. Finally, our conclusion indicated view regarding intermolecular interactions in these mixtures.

3.3. Prigogine-Flory-Patterson Theory:

The applicability of the Prigogine-Flory-Patterson theory (PFP) to predict excess molar volume of binary mixtures of benzylalcohol with isomeric cresols has also been tested. This theory has been described earlier [47, 48].

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The V^E was calculated by means of the PFP theory using the following equation with the three contributions:

$$\frac{V^E}{x_1V_1^*+x_2V_2^*} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}\Psi_1\theta_2\chi_{12}}{[\left(\frac{4}{3}\right)\tilde{V}^{-\frac{1}{3}}-1]P_1^*} \text{ (int.contribution) } + \frac{-(\tilde{V}_1-\tilde{V}_2)[(14/9)\tilde{V}^{-1/3}-1]\Psi_1\Psi_2}{[\left(\frac{4}{3}\right)\tilde{V}^{-\frac{1}{3}}-1]\tilde{V}} \text{ (fv.contribution) } + \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)\Psi_1\Psi_2}{P_2^*\Psi_1+P_1^*\Psi_2} \text{ (}P^*\text{contribution)} \quad (10)$$

The reduced volume of pure component $\tilde{V}_i$ was calculated from the isobaric thermal expansively α_i by equation:

$$\tilde{V}_i = (\frac{1+\left(\frac{4}{3}\right)\alpha_i T}{1+\alpha_i T}) \quad (11)$$

The $\tilde{V}$ of mixture is approximated in equation (12) by $\tilde{V} = \Psi_1\tilde{V}_1 + \Psi_2\tilde{V}_2$ (12)

The molecular contact energy fraction of components Ψ_1 is given by

$$\Psi_1 = 1 - \Psi_2 = \frac{\phi_1P_1^*}{\phi_1P_1^*+\phi_2P_2^*} \quad (13)$$

The characteristic volume is $V_i^* = V_i^*/\tilde{V}_i$ and the characteristic pressure is given by

$$P_i^* = \frac{T\tilde{V}_i^2\alpha_i}{\kappa_{Ti}} \quad (14)$$

where κ_{Ti} is the isothermal compressibility of pure component *i.*

The hard-core volume fractions of the components 1and 2 ($\phi_1$andϕ_2) are defined by

$$\phi_1 = 1-\phi_2 = \frac{x_1V_1^*}{x_1V_1^*+x_2V_2^*} \quad (15)$$

The κ_T values calculated from the fallowing expression,

$$\kappa_T = \kappa_S + \frac{TV\alpha^2}{C_P} \quad (16)$$

The above terms described in the literature [49-51]. The interaction parameter **χ** required for the calculation of V^E using PFP theory has been derived by fitting the experimental V^E values to equation (10) over the whole composition range. The values of three PFP contributions (interactional, free volume and internal pressure), experimental and calculated (using PFP theory)

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V^E values at near equimolar ratio along with pure data of some parameters are given in Tables 8 and 9. An examination of V^E values from PFP theory about (benzylalcohol and isomeric cresol) binary liquid mixtures give good agreement between the experimental and theoretical values.

3.4. Experimental and computational details of FT-IR Studies:

FT-IR spectroscopy has been extensively used to study an intermolecular hydrogen bonding interactions between the binary liquid mixture of benzylalcohol and isomeric cresols more precisely. Generally, intermolecular hydrogen bonds give rise to broad band. Pure liquids show only the broad band in the 3600-3200 cm^{-1}range (hydrogen bonded –OH)[52]. In the present investigation experimental FT-IR spectrum considered at room temperature and equimolar concentration of the resultant absorption bands of the pure components, namely *o*-cresol, *m*-cresol, *p*-cresol and benzylalcohol exhibit some characteristic absorption peaks at 3395 cm^{-1} (O–Hstr), 3328cm^{-1} (0–H str), 3319 cm^{-1} (O-H str) and 3313 cm^{-1} (O-H str) respectively. Further, the resultant absorption bands of binary liquids having hydrogen bonded –OH stretching frequencies i.e., benzylalcohol with *o*-cresol, *m*-cresol, *p*-cresol are 3332 cm^{-1}, 3319 cm^{-1}and 3309cm^{-1} respectively. The value of the O-H stretching frequency has been used as a test of and measures of the strength of hydrogen bonds are shown in Figures S1-S3. The hydrogen bonding length can be considered as a best elucidation of the strength of hydrogen bonding. The comparisons of experimental and theoretical FT-IR wave numbers which are represented in Table 10 suggest that the theoretical values are in good agreement with the experimental values. Moreover, the experimental and theoretical data of FT-IR Spectroscopy indicate that, the existence of the strong intermolecular hydrogen bonded between benzylalcohol and o-cresol mixture due to longer the OH bond, thereby shift the band to higher vibrational frequency (higher energy). Weak intermolecular hydrogen bonding is prevailing in the binary mixtures of benzylalcohol with m-cresol and *p*-cresol leading to shift the O-H band to lower frequency (lower energy).

3.5. Study of hydrogen bond Interaction interms of Density Functional Theory (DFT):

The method of geometrical optimization, determination of interaction energy and natural bonding orbital (NBO) analysis were estimated using density functional theory (DFT) by adopting well known hybrid method (B3LYP)[53]. Since, polarity of molecule has significant role on intermolecular hydrogen bonding. The augmented split valence 6-311++G (d, p) model is used for detailed account of geometrical optimization and natural bonding orbital (NBO) analysis. The above said calculations were performed by employed Gaussian 09 software. Interaction

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energies (ΔE) for the binary mixtures of hydrogen-bonded complex were calculated in terms of the difference between the energy of the hydrogen bonded complex and the summation of the energies of the component molecule as given below:

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

where $E_{complex}$ and $E_{component}$ are optimized energy of the hydrogen bonded complex and individual component molecules. Interaction energies are corrected for the basis set superposition error (BSSE) by counterpoise method [54]. Moreover, the NBO data is a reliable tool for the rationalization of H-bonds that correlate changes in bond length between component molecules. This also provides valuable information on the changes of charge densities of proton donor and acceptor as well as in the bonding and antibonding orbitals. For each donor and acceptor, the stabilization energy E (2) associated with hydrogen bonding between sites i and j are given below

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

where q_i is the i^{th} donor orbital frequency, ε_i, and ε_j are the diagonal elements in connection with NBO Fock matrix. The stabilization energy between lone pair electrons (n) of the proton acceptor and anti-bonding orbitals (σ*) of the proton donor were compared for various intermolecular hydrogen bonding complexes [55–57].

An examination of ten different intermolecular hydrogen bonding complexes between benzylalcohol and isomeric cresols suggest that the existences of intermolecular association in the studied binary mixtures are shown in Table S3 and Figure S4, respectively. The geometrical optimized structures of all the dimers are successfully obtained at the B3LYP/6-311++G (d, p) level. The molecular graphical analysis suggests that different types of hydrogen bonds are formed in the obtained association between the donor (X-H) and acceptor (Y) groups. The change of the X-H bond length during the process of the formation of the hydrogen bond association can throw back the characteristic nature of the H-bond. As shown in Table S3, all the values of ΔR (X-H) of hydrogen bonds are positive and these values reveal that they are all red shifting hydrogen bonds. Furthermore a hydrogen bond parameter ΔR (H…Y) [58], is defined as ΔR (H … Y) = R $(H)_{vwr}$ + $R(Y)_{vwr}$ − R(H …. Y) where $R(Y)_{vwr}$ and $R(H)_{vwr}$ are the van der Waals radii of the H and Y acceptor atoms obtained by Bondi [59] respectively; R(X…Y) is the distance between the hydrogen-donor and hydrogen-acceptor. The ΔR (H … Y) can be estimated as the strength of the hydrogen bond. An examination of Table 6 the largest value of ΔR (H …Y) is 0.8766 A^0, is an indication of the intermolecular O-H ….. O hydrogen bond in the cross-association Va which represents the strongest hydrogen bond. The strength of the hydrogen bond

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in the self and cross-association of all the pure liquids and their mixtures are presented in the following order:

Va (O2-H13…O1) >VIa (O2-H13…O1) >VIIa (O2-H13…O1) >I (O2-H16…O1) > III (O2-H16…O1) > IV (O2-H16…O1) > II (O2-H16…O1) > VII (O1-H8…O2) >VI (O1-H8…O2) >V (O1-H8…O2).

The counterpoise-corrected interaction energies, ΔE^{cp} for all the dimers were computed at DFT, B3LYP with basis set 6-311++G (d, p) and the corrected interaction energies are listed in Table S5 [60]. A perusal of interaction energy data in Table S5 resemble to the results of geometrical structures. In the cross-association of hydrogen bonded complexes, the interaction energy is strong in the dimer Va with O-H … O, whose interaction energy is -33.7180 kJ.mol^{-1}which is higher than that remaining after all other cross-associated dimers.

Therefore, in the cross-associations the O … H-O hydrogen bonds between oxygen atom in OH group of benzylalcohol and hydrogen atom of OH group of isomeric cresols are stronger than the O-H…O hydrogen bond in hydrogen atom of OH group of benzylalcohol and oxygen atom of isomeric cresol mixtures. This can be explained qualitatively by the fact that benzylalcohol acts as a good proton accepter towards the –OH groups of the cresols (proton donor).

In the present study, the NBO analysis has been performed using DFT method to further probe and to investigate the relative strength of all hydrogen bonded dimers. The oxygen atom with a lone pair acts as the donor and H as the acceptor in the strong intermolecular charge transfer interaction. The stabilization energies E (2) of intermolecular interactions of all dimers were executed by applying second order perturbation theory. The stabilization energies between lone pair electrons of the proton acceptor and anti-bonding orbitals of the proton donor were scrutinised for various inter molecular hydrogen bonds of self-association and cross-association at the B3LYP/6-311++G(d, p) level theory and tabulated in Table S6. It is eminence to note that there is a correlation between hydrogen bond length and stabilization energy E (2), i.e., the shorter the bond length (strong hydrogen bond) the larger the stabilization energy [61]. In the case of cross-association effect, the stabilization energy is more in benzylalcohol and *o*-cresol than the benzylalcohol and *m*-cresol and *p*-cresol mixtures are given in Table S6.

According to the computational report on the interaction energies, stabilization energies and geometries reveal that intermolecular cross-associated interactions are much powerful than the intermolecular self-associated interactions between the monomers.

3.6. Structure and electron density analysis:

Moreover, a perusal of the non-covalent intermolecular interactions proposed by Yang and co-worker [62], indicates the plots in Figure 5 the reduced density gradient versus sign (λ2) ρ and the

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reduced density gradient isosurface with s = 0.50 a. u. of the three associations are operative the typical character of sharp spike(s) of weak intermolecular interactions in the low-density region of component molecules. In conformity, the associations of topological properties are shown in Table S4. Apart from this, the reduced density gradient isosurfaces reveal a productive visualization of non-covalent interactions as the broad regions in real space. For three associations employed, it is possible to obtain the strong H-bonds, weaker H-bonds and weaker repulsive interactions accordingly on the gradient isosurfaces.

Resultant plots reveal that, as anticipated, a blue bonding isosurface lies between hydrogen donor of hydroxyl group of benzylalcohol and oxygen acceptor of cresol, is the characteristic sign of strong hydrogen H-bond, and a green bonding isosurface locates between hydrogen donor of hydroxyl group and oxygen acceptor, basic sign of weak inter molecular H-bond. Simultaneously an olive non-bonded overlap isosurface appears between the two monomers give back intermolecular weak steric repulsive interaction. The overall result of the gradient isosurface plot analysis is completely consistent with that of the scatter diagram.

Finally, an examination of the gradient isosurfaces, the intermolecular dispersion interactions of the cross-associations are larger in benzylalcohol and *o*-cresol than the benzylalcohol when compared with *m*- and *p*-cresols.

4. Conclusions:

In this work, we report experimental data for density and speed of sound of benzylalcohol with *o*-cresol, or *m*-cresol or *p*-cresol binary mixtures at temperatures between 303.15K to 323.15K and 303.15K to 313.15K respectively. The experimental excess volume data analyzed in terms of Redlich–Kister and Hwang et al. equations, and measured speed of sound data were compared with theoretical models (FLT, CFT). The experimental V^E data were compared with PFP theory which gives good estimation. A perusal of the relative root mean deviation (RMSD) and mean percentage deviation (MPD) between the experimental and the theoretical values of speed of sound showed a better prediction using the CFT. The interaction is stronger in case of benzylalcohol and *o*-cresol mixture when compared to benzylalcohol and *m*-cresol / *p*-cresol mixtures. The results were analyzed by experimental and theoretical FT-IR. The thermodynamic properties of benzylalcohol with isomeric-cresol mixtures are correlated by the interplay of specific interactions in hydrogen bonding with FT-IR Spectra. The excess thermodynamic properties can be interpreted by considering the intermolecular hydrogen bonding, molecular size and shapes of the components. To verify hydrogen bond formation and to better explore hydrogen bond interaction between benzylalcohol and isomeric cresol and ten different associations of these

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component molecules are successfully optimized at the B3LYP/6-311++G(d, p) level. The computational extended analysis is in good agreement with the experimental data.

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References:

[1] R. Aguado, M. Olazar, M.J.S. Jose, G. Aguirre, J. Bilbao, *Ind. Eng. Chem. Res*, 2000, **39**, 1925−1933.

[2] M. Bertero, G. de la Puente, U. Sedran, *Fuel*, 2012, **95**, 263−271.

[3] L. Venkatramana, K.Sivakumar, R.L. Gardas, K.Dayananda Reddy, *Thermochim.Acta.*2014, **581**, 123-132.

[4] W.Martindale, The Extra Pharmacopoeia,33rd ed. Pharmaceutical Press,London,2002.

[5] Kai-Di Chen, Yi-Feng Lin, Chein-HsiuTu, *J.Chem. Eng.Data*. 2012, **57**, 1118–1127.

[6] The Merck Index, 33rd ed. Merck and Co. Inc, Wiley Interscience, New York, 2001.

[7] S.N.Shrivastav, J.D. Pandey, *Acoustics lett*., 1982-83, **6**, 9.

[8] C.V.Surya Narayana, P. Puyazhendhi, *Ind. J. Tech.* 1990, **28**, 120–124.

[9] W.Schaffs, Z.Med.Phy.,1940, **115**,69-75.

[10] B. Jacobson, *Acta.Chem.Scand.,*1952, **6**, 1485-1498.

[11] B. Jacobson, *J.Chem. Phys*.,1952, **20**, 927-928.

[12] S.L. Oswal, V. Pandiyan, B. Krishnakumar, P. Vasantharani, *Thermochim. Acta.,*2010, **507–508**, 27–34.

[13] Yu-Feng Zhang, Rong-Yi Huang, Jun-Wei Wang, Xue-Jun Kong, *RSC Adv.*, 2015, DOI: 10.1039/C5RA09071G.

[14] J.A. Riddick, W. Bunger, T.K. Sakano, Fourth ed. Wiley Interscience, New York, 1986.

[15] M. Raveendra, C.Narasimharao, L.Venkatramana,K.Sivakumar, K.DayanandaReddy, *J. Chem. Thermodyn*., 2016, **92**, 97–107.

[16] L. Venkatramana, C. NarasimhaRao, R.L.Gardas, K.Sivakumar, *J. Mol. Liq.*, 2015,**207**, 171–176.

[17] A. Ali, M. Tariq,*J. Mol. Liq.*, 2006, **128**, 50–55.

[18] L.Venkatramana, R.L. Gardas, K.Sivakumar, K.Dayananda Reddy, *Fluid Phase Equilib.,* 2014, **367**, 7-21.

RSC Advances Accepted Manuscript

[19] R. Francesconi, A.Bigi, K.Rubini, F.Comelli, *J. Chem. Eng. Data.,* 2005, **50**, 1932–1937.

[20] A.Ali, A.K. Nain, D. Chand, R. Ahmad, *Phys. Chem. Liq*., 2005, **43**, 205–224.

[21] R.L. Gardas, J.A.P.Coutinho, *Fluid Phase Equilib*., 2008, **267**, 188–192.

[22] D.L. Cunha, J.A.P.Coutinho, Jean Luc.Daridon, R.A.Reis,Marcio L.L.Paredes, *J. Chem. Eng. Data*.,2013, **58**, 2925−2931.

[23] S. C. Bhatia, R. Rani, R. Bhatia, *J. Chem. Eng. Data*.,2011, **56**, 1669−1674.

[24] M. Klauck, A. Grenner, K. Taubert, A. Martin, R. Meinhardt, J. Schmelzer, *Ind. Eng. Chem. Res.,*2008, **47**, 5119−5126.

[25] S.C. Bhatia, R.Rani, R. Bhatia, H.Anand, *J. Chem. Thermodyn*., 2011, **43**, 479−486.

[26] J.A. Riddick, W.B. Bunger, 3rd ed., *Wiley Interscience*, New York,1970.

[27] K. Narendra, C. Srinivasu, S.Fakruddin, P.Narayanamurthy, *J. Chem. Thermodyn*., 2011, **43**, 1604−1611.

[28] H. Stage, E. Mueller, P.Faldix, *ErdoelKohle.* 1953, **6**, 375−380.

[29] C. Yang, W.Yu, D. Tang, *J. Chem. Eng. Data*., 2006, **51**, 935−939.

[30] J.S. Chang, M.J. Lee, *J. Chem. Eng. Data*., 1995, **40**, 1115−1118.

[31] A.D. Becke, *Phys. Rev. A.,* 1988, **38**, 3098-3100.

[32] A.D. Becke, *J. Chem.Phys*., 1993, **98**,5648–5652.

[33] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B.,*1988, **37**, 785–789.

[34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. V. reven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D. 01, Gaussian, Inc., Wallingford, CT, 2013.

[35] A. Saleh Mohammad , Shahanara Begum, M.H.Uddin, *J. Mol. Liq*.,2001,**94**, 155-161.

[36] V. Syamala, P.Venkateswarlu, K.Sivakumar, *J.Chem.Eng.Data*.,2006, **51**, 928-934.

[37] T.M. Aminabhavi, L.S. Manjeshwar, S.S. Joshi, S.B. Halligudi and R.H. Balundgi, *Indian J. Chem.,* 1988, 27A, 721 – 724.

RSC Advances Accepted Manuscript

[38] G. Douhéret, M.I. Davis, J.C.R. Reis, M.J. Blandamer, *Chem Phys Chem.*, 2001, **2**, 148-161.

[39] G.C. Benson, O.Kiyohara, *J. Chem. Thermodyn.,* 1979, **11**, 1061-1064.

[40] M. Yasmin, K.P. Singh, S.Parveen, M. Gupta, J.P. Shukla, *Acta Physica Polonica A.,* 2009, **115**, 890-900.

[41] T.J. Bruno, M.L. Huber, A. Laesecke, E.W. Lemmon, R.A. Perkins, NIST IR 6640; National Institute of Standards and Technology (NIST): Boulder, CO, 2006.

[42] A. R. H. Goodwin, K.N. Marsh, W.A. Wakeham, Experimental Thermodynamics; IUPAC, Elsevier: The Netherlands, 2003; Vol. **VI**.

[43] A. Ali, A.K. Nain, *Bull. Chem. Soc. Jpn*., 2002, **75**, 681-687.

[44] O. Redlich, A.T.Kister. *J.Ind.Eng.Chem*., 1948, **40**, 345-348.

[45] C.A. Hwang, J.C. Holstc, K.R. Hall, G.A.Mansoori, *Fluid Phase Equilib.,* 1991, **62**, 173-189.

[46] L. Venkatramana, R. L. Gardas, C. Narasimha Rao, K. Sivakumar, K. Dayananda Reddy, *J. Solution. Chem*. 2015, **44**, 327–359.

[47] S.L. Oswal, S.G.Patel, R.L. Gardas, N.Y. Ghael, *Fluid Phase Equilib*., 2004, **215**, 61-70.

[48] V. Syamala, L.Venkatramana, C.Narasimha Rao, K.Sivakumar, P.Venkateswarlu, R.L. Gardas, *Fluid Phase Equilib*., 2015, **397**, 68-80.

[49] A. Abe, P.J. Flory, *J.Am.Chem.Soc*., 1965,**87**, 1838-1846.

[50] P.J. Flory, *J.Am.Chem.Soc*., 1965, **87**, 1833-1838.

[51] I. Prigogine. Molecular Theories of Solutions, North-Holland Publishing, Amsterdam, 1957.

[52] R.M. Silverstein, G.C. Bassler, T. C. Morrik, Spectroscopic Identification of Organic Compounds, 5thedn. John Wiley& sons, Inc., Singapore, 1991.

[53] M. Chandra Sekhar, M.GowriSankar, A.Venkatesulu, *J. Mol. Liq.,* 2015, **209**, 428–439.

[54] S.F. Boys, F. Bernardi, *Mol. Phys.,* 1970, **19**, 553–566.

[55] F. Weinhold, C.R. Landis, Chem. Educ. Res. Pract., 2001, **2**, 91–104.

[56] E.D. Gledening, A.E. Reed, J.A. Carpenter, F. Weinhold, NBO. *Version 3.1*.

[57] A.E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*1988, **88**, 899–926.

[58] Chang Guo, Hui Fang, Rong-Yi Huang, HengXu, Gen-Hua Wu, Shi-Yong Ye, *Chem.Phys.Lett.,* 2013, **588**, 97–101.

[59] A. Bondi, *J. Phys. Chem*.,1964, **68**, 441–451.

[60] R.Y. Huang, R. B. Du, G. X. Liu, X. Q. Zhao, S. Y. Ye, G.H. Wu, *J. Chem. Thermodyn.*,2012, **55**, 60–66.

[61] S. Pal, T.K.Kundu*, ISRN Phys. Chem.,* 2012, **2012**, 1–12.

RSC Advances Accepted Manuscript

[62] E.R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A.J. Cohen, W.T. Yang, *J. Am. Chem. Soc.,*2010, **132**, 6498.

Figure captions:

Figure 1:

Variation of excess volume (V^E) of the binary liquid mixture of benzylalcohol (1) with *o*-cresol (2) (■), m-cresol (2) (●), *p*-cresol (2) (▼), at 303.15 K.

Figure 2:

Variation of excess volume (V^E) of the binary liquid mixture of benzylalcohol (1) with *o*-cresol (2) (■), *m*-cresol (2) (●), *p*-cresol (2) (▼), at 313.15 K.

Figure 3:

Variation of excess isentropic compressibility (κ_s^E) of the binary liquid mixture of benzylalcohol (1) with *o*-cresol (2) (■), *m*-cresol (2) (●), *p*-cresol (2) (▼), at 303.15 K.

Figure 4:

Variation of excess isentropic compressibility (κ_s^E) of the binary liquid mixture of benzylalcohol (1) with *o*-cresol (2) (■), *m*-cresol (2) (●), *p*-cresol (2) (▼), at 313.15 K.

Figure 5:

Plots of the reduced density gradient versus the electron density multiplied by the sign of the second hessian eigenvalues and gradient isosurfaces with s = 0.5 a.u. for the associations of Benzylalcohol with *o, m, p-* cresols (fig 5 (a1), 5 (a2): fig 5 (b1), 5 (b2) and fig 5 (c1), 5 (c2)) respectively. The surfaces are colored on a blue–green–red scale according to values of sign (λ2) ρ, ranging from -0.03 to 0.02 a. u.

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Table 1: Name of the chemical, source, CAS number, purity in mass fraction, purity analysis method and water content in mass fraction of the chemicals used in this work.

Component	Source	CAS number	Purity in mass fraction (as received from supplier	Purity in mass fraction (after purification)	*Analysis method	Water content in mass fraction
Benzylalcohol	S.D.Fine Chemicals. Ltd.	100-51-6	0.995	0.996	GC	0.0005
o-Cresol	S.D.Fine Chemicals. Ltd	95-48-7	0.99	0.994	GC	0.0007
m-Cresol	S.D.Fine Chemicals. Ltd	108-39-4	0.98	0.994	GC	0.0008
p-Cresol	S.D.Fine Chemicals. Ltd.	106-44-5	0.985	0.997	GC	0.0005

*GC=Gas Chromatography

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Table 2: Density (ρ) and sound speed (u) values for the pure components along with literature values at temperatures studied and at 0.1 MPa pressure.

T/K	ρ/(g.cm^{3})		u/(m.s^{-1})	
	Exp.	Lit.	Exp.	Lit.
	Benzylalcohol			
303.15	1.03715	1.03700[17] 1.03767[18]	1514	1511[17] 1514[18]
308.15	1.03332	1.03366[19]	-	-
313.15	1.02946	1.02920[20]	1485	1484[21]
318.15	1.02554	-	-	-
323.15	1.02171	-	-	-
	o-cresol			
303.15	1.03701	1.037046[22] 1.0369[23]	1488	1488.19[22] 1487[23]
308.15	1.03264	1.032642[22]	-	-

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		1.03273[24]		
313.15	1.02824	1.028145[25] 1.0282[26]	1452	1452.65[22] 1452.11[27]
318.15	1.02377	1.023825[22] 1.0211[27]	-	-
323.15	1.01935	1.019387[22] 1.0198[28]	-	-
		m-cresol		
303.15	1.02524	1.025959[22] 1.0261[23]	1466	1466.16[22] 1465[23]
308.15	1.02127	1.021988[22] 1.0215[27]	-	-
313.15	1.01727	1.0170[27] 1.01763[29]	1435	1439.97[22] 1439.56[25]
318.15	1.01348	1.0135[27] 1.01360[29]	-	-

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323.15	1.00921	1.00956[29] 1.0098[30]	-	-
		p-cresol		
303.15	1.02650	1.02639[22] 1.0263[23] 1.0265[27]	1471	1471.38[22] 1471[23] 1468.43[27]
308.15	1.02258	1.02250[22] 1.0225[28]	-	-
313.15	1.01870	1.018593[22] 1.0188[24]	1439	1439.97[22] 1439.56[25]
318.15	1.01471	1.014661[22] 1.0139[27]	-	-
323.15	1.01078	1.010701[22] 1.0102[28]	-	-

The standard uncertainties are u (ρ) = 2*x* 10^{-3} g. cm^{-3}, u (u) = 0.3%, u (T) = 0.01 K for density, u (T) = 0.02 K for speed of sound and u (p) = 1 kPa.

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Table 3: Mole fraction of benzylalcohol (x_1), densities (ρ), experimental excess volumes (V^E) and predicted excess volumes (Redlich-Kister &Hwang) at T= 303.15 K to 323.15 K and 0.1M Pa pressure for the binary mixtures of benzylalcohol with *o, m, p*-cresols.

x_1	Density(ρ) ($g.cm^{-3}$)	V^E / cm^3mol^{-1}		
		Exp.	Redlich-Kister	Hwang
Benzylalcohol (1) + *o*-cresol (2)				
T=303.15 K				
0.0834	1.03714	-0.012	-0.012	-0.012
0.1667	1.03728	-0.025	-0.024	-0.024
0.2501	1.03739	-0.035	-0.034	-0.034
0.3334	1.03747	-0.042	-0.042	-0.042
0.4168	1.03753	-0.046	-0.047	-0.047
0.5001	1.03755	-0.047	-0.049	-0.048
0.5834	1.03755	-0.046	-0.047	-0.047
0.6668	1.03752	-0.042	-0.042	-0.042

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0.7501	1.03746	-0.035	-0.034	-0.034
0.8334	1.03738	-0.025	-0.023	-0.023
0.9167	1.03726	-0.012	-0.012	-0.012
		T = 308.15 K		
0.0834	1.03283	-0.014	-0.014	-0.014
0.1667	1.03303	-0.028	-0.027	-0.027
0.2501	1.03319	-0.039	-0.038	-0.038
0.3334	1.03332	-0.046	-0.047	-0.047
0.4168	1.03343	-0.051	-0.052	-0.052
0.5001	1.03350	-0.053	-0.054	-0.053
0.5834	1.03354	-0.051	-0.052	-0.052
0.6668	1.03356	-0.047	-0.046	-0.046
0.7501	1.03354	-0.039	-0.038	-0.038
0.8334	1.03348	-0.028	-0.027	-0.027
0.9167	1.03339	-0.013	-0.014	-0.014
		T=313.15 K		
0.0834	1.02849	-0.015	-0.016	-0.016

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0.1667	1.02876	-0.032	-0.030	-0.030
0.2501	1.02896	-0.042	-0.042	-0.042
0.3334	1.02915	-0.051	-0.051	-0.051
0.4168	1.02930	-0.056	-0.057	-0.057
0.5001	1.02942	-0.058	-0.059	-0.059
0.5834	1.02950	-0.056	-0.057	-0.057
0.6668	1.02955	-0.051	-0.052	-0.051
0.7501	1.02958	-0.043	-0.043	-0.043
0.8334	1.02957	-0.032	-0.031	-0.031
0.9167	1.02952	-0.016	-0.016	-0.016
		T=318.15 K		
0.0834	1.02410	-0.018	-0.018	-0.018
0.1667	1.02441	-0.035	-0.035	-0.035
0.2501	1.02470	-0.049	-0.048	-0.048
0.3334	1.02495	-0.059	-0.058	-0.058
0.4168	1.02516	-0.065	-0.065	-0.065
0.5001	1.02532	-0.066	-0.067	-0.067

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0.5834	1.02546	-0.064	-0.065	-0.065
0.6668	1.02556	-0.059	-0.059	-0.059
0.7501	1.02562	-0.05	-0.050	-0.049
0.8334	1.02564	-0.037	-0.036	-0.036
0.9167	1.02563	-0.019	-0.019	-0.019
T=323.15 K				
0.0834	1.01976	-0.022	-0.022	-0.022
0.1667	1.02016	-0.043	-0.042	-0.042
0.2501	1.02051	-0.059	-0.059	-0.059
0.3334	1.02082	-0.071	-0.071	-0.070
0.4168	1.02108	-0.078	-0.079	-0.078
0.5001	1.02130	-0.08	-0.081	-0.081
0.5834	1.02148	-0.078	-0.079	-0.079
0.6668	1.02161	-0.071	-0.071	-0.071
0.7501	1.02170	-0.06	-0.059	-0.059
0.8334	1.02174	-0.044	-0.043	-0.042

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0.9167	1.02173	-0.022	-0.023	-0.023
Benzylalcohol (1) + *m*-cresol (2)				
T=303.15 K				
0.0867	1.02633	-0.007	-0.007	-0.007
0.1728	1.02740	-0.012	-0.012	-0.012
0.2582	1.02845	-0.016	-0.017	-0.016
0.3431	1.02948	-0.019	-0.020	-0.019
0.4273	1.03050	-0.021	-0.021	-0.021
0.5109	1.03151	-0.022	-0.022	-0.022
0.5939	1.03249	-0.021	-0.021	-0.021
0.6763	1.03345	-0.019	-0.018	-0.020
0.7581	1.03440	-0.016	-0.015	-0.017
0.8393	1.03533	-0.011	-0.011	-0.013
0.9199	1.03624	-0.005	-0.006	-0.008
T=308.15 K				
0.0867	1.02240	-0.010	-0.009	-0.009
0.1728	1.02347	-0.014	-0.015	-0.015

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0.2582	1.02453	-0.018	-0.019	-0.019
0.3431	1.02558	-0.021	-0.021	-0.021
0.4273	1.02661	-0.023	-0.022	-0.022
0.5109	1.02763	-0.024	-0.023	-0.023
0.5939	1.02862	-0.023	-0.022	-0.022
0.6763	1.02959	-0.021	-0.021	-0.021
0.7581	1.03056	-0.018	-0.019	-0.019
0.8393	1.03150	-0.014	-0.015	-0.015
0.9199	1.03244	-0.010	-0.009	-0.009
		T=313.15 K		
0.0867	1.01842	-0.011	-0.011	-0.011
0.1728	1.01951	-0.016	-0.017	-0.017
0.2582	1.02058	-0.020	-0.021	-0.020
0.3431	1.02164	-0.023	-0.022	-0.022
0.4273	1.02268	-0.024	-0.023	-0.023
0.5109	1.02370	-0.025	-0.024	-0.024
0.5939	1.02471	-0.024	-0.023	-0.023

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0.6763	1.02570	-0.022	-0.022	-0.022
0.7581	1.02668	-0.020	-0.021	-0.021
0.8393	1.02764	-0.016	-0.017	-0.017
0.9199	1.02858	-0.011	-0.010	-0.010
		T=318.15 K		
0.0867	1.01463	-0.012	-0.012	-0.012
0.1728	1.01572	-0.018	-0.019	-0.019
0.2582	1.01679	-0.022	-0.023	-0.023
0.3431	1.01784	-0.025	-0.025	-0.025
0.4273	1.01888	-0.027	-0.026	-0.026
0.5109	1.01990	-0.028	-0.027	-0.027
0.5939	1.02090	-0.027	-0.026	-0.026
0.6763	1.02188	-0.025	-0.025	-0.025
0.7581	1.02285	-0.022	-0.023	-0.023
0.8393	1.02380	-0.018	-0.019	-0.019
0.9199	1.02473	-0.012	-0.012	-0.012
		T=323.15 K		

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0.0867	1.01041	-0.014	-0.013	-0.013
0.1728	1.01154	-0.020	-0.021	-0.021
0.2582	1.01264	-0.024	-0.025	-0.025
0.3431	1.01372	-0.027	-0.027	-0.027
0.4273	1.01479	-0.029	-0.028	-0.028
0.5109	1.01584	-0.030	-0.029	-0.029
0.5939	1.01687	-0.029	-0.028	-0.028
0.6763	1.01789	-0.027	-0.027	-0.027
0.7581	1.01889	-0.024	-0.025	-0.025
0.8393	1.01987	-0.020	-0.021	-0.020
0.9199	1.02082	-0.013	-0.013	-0.013
Benzylalcohol (1) + *p*-cresol (2)				
T=303.15 K				
0.0838	1.02733	0.006	0.006	0.006
0.1675	1.02819	0.008	0.008	0.008
0.2511	1.02909	0.007	0.007	0.007
0.3346	1.02999	0.005	0.005	0.005

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0.4181	1.03091	0.002	0.002	0.001
0.5015	1.03184	-0.003	-0.002	-0.002
0.5848	1.03276	-0.006	-0.006	-0.005
0.6680	1.03367	-0.008	-0.008	-0.008
0.7511	1.03457	-0.009	-0.009	-0.009
0.8341	1.03545	-0.008	-0.009	-0.009
0.9171	1.03632	-0.006	-0.006	-0.006
		T=308.15 K		
0.0838	1.02339	0.008	0.008	0.009
0.1675	1.02426	0.011	0.011	0.011
0.2511	1.02516	0.010	0.010	0.010
0.3346	1.02607	0.008	0.007	0.007
0.4181	1.02699	0.005	0.003	0.003
0.5015	1.02796	-0.002	-0.001	-0.001
0.5848	1.02888	-0.005	-0.004	-0.004
0.6680	1.02980	-0.007	-0.007	-0.006
0.7511	1.03070	-0.008	-0.008	-0.007

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0.8341	1.03159	-0.002	-0.007	-0.007
0.9171	1.03246	-0.004	-0.004	-0.005
T=313.15 K				
0.0838	1.01951	0.009	0.009	0.010
0.1675	1.02037	0.012	0.012	0.012
0.2511	1.02127	0.011	0.011	0.011
0.3346	1.02219	0.009	0.008	0.008
0.4181	1.02311	0.006	0.004	0.004
0.5015	1.02408	-0.001	0.000	0.000
0.5848	1.02500	-0.004	-0.004	-0.003
0.6680	1.02592	-0.006	-0.006	-0.005
0.7511	1.02683	-0.007	-0.007	-0.006
0.8341	1.02772	-0.006	-0.006	-0.006
0.9171	1.02859	-0.003	-0.003	-0.004
T=318.15K				
0.0838	1.01552	0.010	0.010	0.011
0.1675	1.01637	0.015	0.014	0.015

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0.2511	1.01729	0.014	0.014	0.014
0.3346	1.01821	0.012	0.011	0.010
0.4181	1.01916	0.007	0.007	0.006
0.5015	1.02012	0.002	0.002	0.002
0.5848	1.02106	-0.002	-0.001	-0.001
0.6680	1.02199	-0.004	-0.004	-0.003
0.7511	1.02291	-0.005	-0.005	-0.004
0.8341	1.02381	-0.004	-0.004	-0.004
0.9171	1.02470	-0.002	-0.002	-0.003
		T=323.15K		
0.0838	1.01156	0.013	0.013	0.013
0.1675	1.01243	0.017	0.018	0.018
0.2511	1.01333	0.018	0.018	0.018
0.3346	1.01426	0.016	0.015	0.014
0.4181	1.01521	0.012	0.010	0.010
0.5015	1.01617	0.006	0.006	0.006
0.5848	1.01713	0.001	0.002	0.002

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0.6680	1.01807	-0.002	-0.001	-0.001
0.7511	1.01900	-0.003	-0.002	-0.002
0.8341	1.01990	-0.002	-0.002	-0.002
0.9171	1.02080	-0.001	-0.001	-0.002

The standard uncertainties are $u\ (X_1) = 1\times10^{-4}$, $u\ (\rho) = 2\times10^{-3}$ g·cm^{-3}, $u\ (T) = 0.01$ K for density, $u\ (p) = 1$ kPa, and u (V^E) = ±0.005 cm^3·mol^{-1}.

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Table 4

Molefraction (x_1) of benzylalcohol, densities(ρ), experimental sound speed(u), isentropiccompressibilities(κ_s), excess isentropic compressibilities (κ_s^E) and predicted excess isentropic compressibilities (Redlich-Kister & Hwang equations) theoretical sound speed values of benzylalcohol (1) with *o, m, p*-cresols (2) at 303.15K and 313.15 K and 0.1M Pa pressure.

x_1	u(exp) (m.s^{-1})	κ_s (TPa^{-1})	u_{FLT} (m.s^{-1})	u_{CFT} (m.s^{-1})	κ_s^E/(TPa^{-1})		
					Exp.	Redlich-Kister	Hwang
				Benzylalcohol (1) + o-cresol (2)			
				T=303.15 K			
0.0834	1490	434.4	1492	1490	0.09	0.09	0.09
0.1667	1492	433.1	1496	1492	0.16	0.16	0.16
0.2501	1494	431.9	1500	1495	0.22	0.21	0.22
0.3334	1496	430.6	1504	1497	0.26	0.25	0.25

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0.4168	1498	429.3	1507	1499	0.28	0.28	0.28
0.5001	1501	427.9	1510	1501	0.29	0.29	0.29
0.5834	1503	426.6	1512	1503	0.28	0.28	0.28
0.6668	1505	425.4	1513	1505	0.26	0.27	0.26
0.7501	1508	424.1	1514	1508	0.22	0.23	0.23
0.8334	1510	422.9	1515	1510	0.17	0.16	0.17
0.9167	1512	421.8	1514	1512	0.10	0.10	0.10
T=313.15 K							
0.0834	1454	459.6	1456	1455	0.08	0.08	0.08
0.1667	1457	457.9	1461	1457	0.14	0.14	0.14
0.2501	1460	456.1	1465	1460	0.19	0.19	0.19
0.3334	1463	454.3	1469	1463	0.23	0.23	0.23
0.4168	1465	452.4	1472	1466	0.25	0.25	0.25
0.5001	1468	450.6	1475	1468	0.26	0.26	0.26
0.5834	1471	448.8	1478	1471	0.25	0.25	0.25
0.6668	1474	447.0	1480	1474	0.24	0.23	0.23
0.7501	1477	445.3	1482	1477	0.20	0.20	0.20

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0.8334	1480	443.6	1483	1479	0.15	0.15	0.15
0.9167	1482	442.0	1484	1482	0.08	0.08	0.08
Benzylalcohol (1)+ m-cresol (2)							
T=303 .15 K							
0.0867	1319	450.8	1453	1470	-0.18	-0.18	-0.18
0.1728	1338	447.8	1444	1474	-0.33	-0.32	-0.32
0.2582	1359	444.9	1436	1478	-0.43	-0.43	-0.43
0.3431	1381	442.0	1432	1482	-0.50	-0.50	-0.51
0.4273	1403	439.2	1430	1486	-0.55	-0.55	-0.55
0.5109	1426	436.4	1430	1490	-0.56	-0.56	-0.56
0.5939	1448	433.7	1434	1494	-0.54	-0.53	-0.54
0.6763	1469	431.0	1442	1498	-0.49	-0.49	-0.49
0.7581	1489	428.3	1453	1502	-0.41	-0.41	-0.41
0.8393	1507	425.7	1468	1506	-0.30	-0.30	-0.30
0.9199	1521	423.2	1488	1510	-0.16	-0.16	-0.16
T=313.15 K							
0.0867	1291	474.0	1426	1439	-0.22	-0.22	-0.22

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0.1728	1308	470.7	1419	1444	-0.38	-0.38	-0.38
0.2582	1325	467.4	1414	1448	-0.50	-0.51	-0.51
0.3431	1342	464.2	1411	1452	-0.59	-0.59	-0.59
0.4273	1360	461.1	1411	1456	-0.64	-0.64	-0.64
0.5109	1379	458.0	1413	1460	-0.65	-0.65	-0.65
0.5939	1398	455.0	1418	1465	-0.63	-0.63	-0.63
0.6763	1417	452.0	1425	1469	-0.57	-0.56	-0.57
0.7581	1437	449.0	1435	1473	-0.48	-0.48	-0.48
0.8393	1456	446.1	1448	1477	-0.36	-0.37	-0.36
0.9199	1476	443.3	1464	1481	-0.20	-0.20	-0.20

Benzylalcohol (1) + p-cresol (2)

T=303.15 K

0.0838	1475	447.7	1472	1475	-0.29	-0.29	-0.29
0.1675	1478	445.1	1474	1478	-0.54	-0.54	-0.54
0.2511	1482	442.6	1477	1481	-0.76	-0.75	-0.76
0.3346	1485	440.1	1480	1485	-0.92	-0.92	-0.92
0.4181	1489	437.6	1483	1489	-1.03	-1.03	-1.03

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0.5015	1492	435.1	1487	1492	-1.09	-1.09	-1.09
0.5848	1496	432.6	1491	1495	-1.08	-1.08	-1.08
0.6680	1500	430.2	1496	1500	-1.01	-1.01	-1.01
0.7511	1503	427.7	1500	1503	-0.87	-0.87	-0.87
0.8341	1507	425.3	1505	1506	-0.66	-0.66	-0.66
0.9171	1510	423.0	1510	1510	-0.37	-0.37	-0.37
T=313.15 K							
0.0838	1443	471.2	1440	1443	-0.33	-0.33	-0.33
0.1675	1447	468.3	1443	1446	-0.63	-0.63	-0.62
0.2511	1450	465.4	1446	1450	-0.88	-0.88	-0.88
0.3346	1454	462.5	1449	1454	-1.07	-1.07	-1.08
0.4181	1458	459.7	1453	1458	-1.20	-1.21	-1.21
0.5015	1462	456.9	1457	1461	-1.28	-1.27	-1.27
0.5848	1466	454.1	1461	1466	-1.27	-1.27	-1.27
0.6680	1470	451.3	1466	1470	-1.18	-1.19	-1.18
0.7511	1473	448.5	1471	1472	-1.02	-1.02	-1.02
0.8341	1477	445.8	1475	1477	-0.77	-0.77	-0.77

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0.9171	1481	443.2	1480	1481	-0.43	-0.43	-0.43

The standard uncertainties are *u* (X_1) = 1×10^{-4}, u (u) = 0.3% *u* (*T*) = 0.02 K for speed of sound and *u* (*p*) = 1 kPa.

Table 5

RMSD & MPD of speed of sound (u) of benzylalcohol with *o, m, p*-cresols (2) at T= 303.15K and 313.15 K from CFT,FLT models.

	RMSD	MPD
Benzylalcohol (1) + o-cresol (2)		
T=303.15K		
CFT	0.0004	0.0182
FLT	0.0045	0.4119
T=313.15K		
CFT	0.0004	0.0186
FLT	0.0036	0.3405
Benzylalcohol (1) + *m*-cresol (2)		
T=303.15K		
CFT	0.0002	0.0062

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FLT	0.0308	2.9272
T=313.15K		
CFT	0.0002	0.0063
FLT	0.0249	2.3646
Benzylalcohol (1) + *p*-cresol (2)		
T=303.15K		
CFT	0.0003	0.0122
FLT	0.0028	0.2563
T=313.15K		
CFT	0.0004	0.0187
FLT	0.0027	0.2492

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Table 6:
Calculated values of the three contributions to the excess molar volume at equimolar concentration from the PFP theory with interaction parameter.

System	T(K)	$\chi\,x10^6$ (J mol^{-1})	$V^E x10^6$ m^{3}mol^{-1}				
			V^E(int)	V^E(fv)	V^E(P*)	Exp	PFP
benzylalcohol+	303.15	-5.524	-0.0508	0.0001	-0.00001	-0.047	-0.051
o-cresol	313.15	-6.254	-0.0601	0.00001	-0.00012	-0.058	-0.060
benzylalcohol+	303.15	-2.137	-0.0201	0.00013	-0.00237	-0.022	-0.023
m-cresol	313.15	-1.723	-0.0169	0.00015	-0.00256	-0.020	-0.020
benzylalcohol+	303.15	-0.268	-0.0025	0.00010	-0.00067	-0.003	-0.003
p-cresol	313.15	0.274	0.0026	0.00011	-0.00083	-0.001	0.002

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Table 7:

Values of molar volume(V), reduced volume($\tilde{V}$), thermal expansion coefficient($\boldsymbol{\alpha}$), heat capacity(C_P), isothermal compressibility (κ_T) and characteristic parameters (P*,V* and T*) for pure liquids.

Liquid	T/K	V ($cm^3 mol^{-1}$)	$\tilde{V}$ ($cm^3 mol^{-1}$)	$10^3\boldsymbol{\alpha}$ (K^{-1})	C_P ($J.K^{-1}.mol^{-1}$)	κ_T (TPa^{-1})	P*	V*	T* (K)
Benzyl	303.15	104.27	1.2017	0.771	224.35	504.45	669.39	86.76	6131.4
alcohol	313.15	105.05	1.2088	0.777	227.62	527.76	673.71	86.90	6180.6
o-cresol	303.15	104.28	1.0632	0.771	236.84	514.95	655.85	86.77	6130.9
	313.15	105.17	1.0653	0.778	245.53	524.48	656.42	86.99	6176.2
m-cresol	303.15	105.48	1.0638	0.780	224.90	540.41	634.27	87.62	6087.7
	313.15	106.30	1.0659	0.786	231.50	566.30	637.62	87.79	6136.2
p-cresol	303.15	105.35	1.0637	0.779	277.80	520.03	658.04	87.53	6092.5
	313.15	106.15	1.0658	0.785	285.12	545.96	660.18	87.68	6141.4

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Table 8:

Experimental and Theoretical FT-IR analysis of the pure and equimolar binary mixture systems at temperature T =298.15 K

Compound	Band	Experimental		Theoretical (DFT - B3LYP) 6-311++G(d,p)	
		υ (cm^{-1})	$\Delta\upsilon$ (cm^{-1})	υ (cm^{-1})	$\Delta\upsilon$ (cm^{-1})
Benzyl alcohol	OH^1	3313	-	3421	
o-cresol	OH^2	3395	-	3372	
m-cresol	OH^3	3328	-	3321	
p-cresol	OH^4	3319	-	3317	
Benzyl alcohol+ *o*-cresol	OH^1- OH^2	3342	29-(OH)	3456	35(OH)
		3375	20-(OH)	3355	17(OH)
Benzyl alcohol+ *m*-cresol	OH^1-OH^3	3331	18(OH)	3449	28(OH)
		3316	12(OH)	3306	15(OH)
Benzyl alcohol+ *p*-cresol	OH^1-OH^4	3327	14-(OH)	3439	18(OH)
		3313	6(OH)	3307	10(OH)

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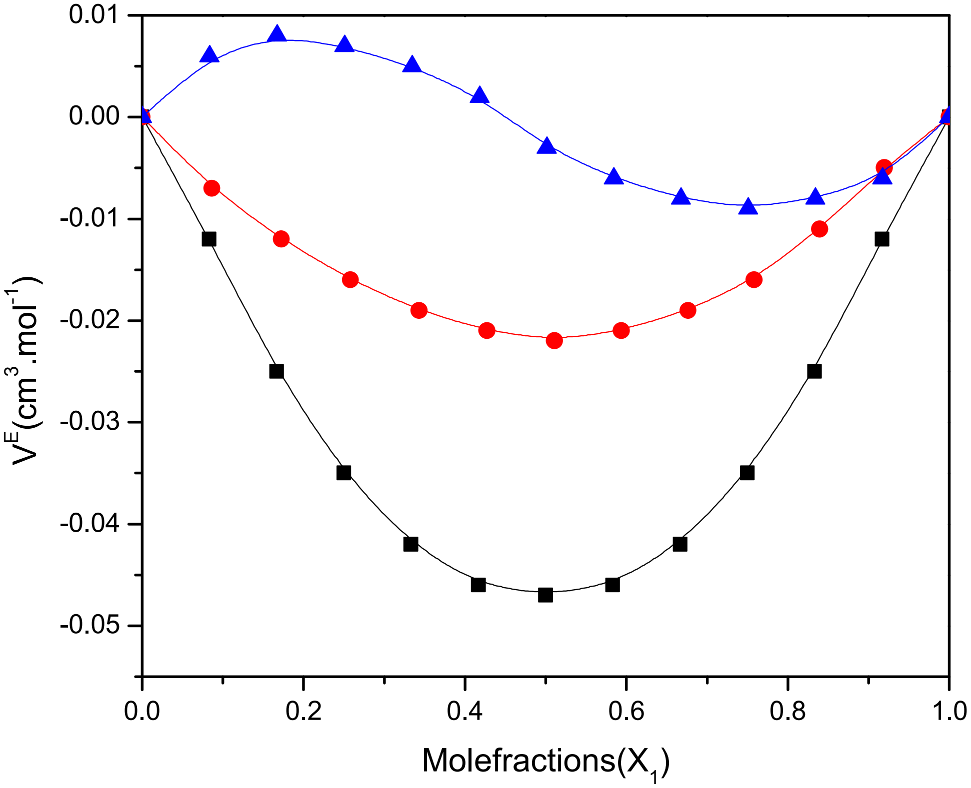

Figure 1

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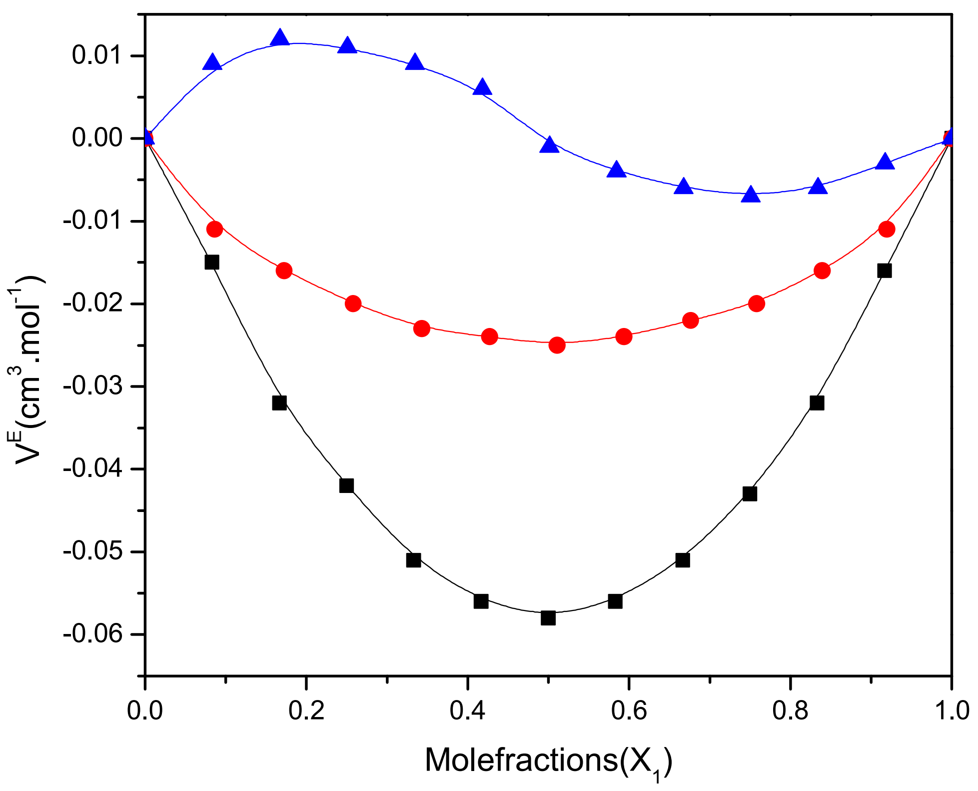

Figure 2

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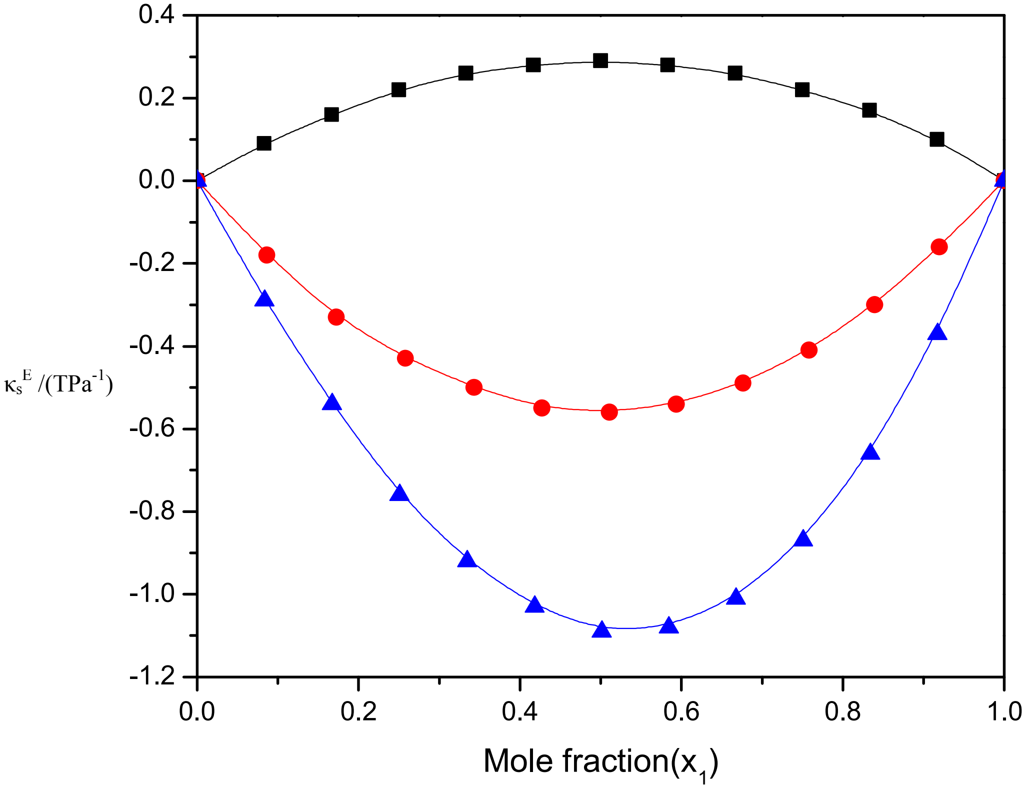

Figure3

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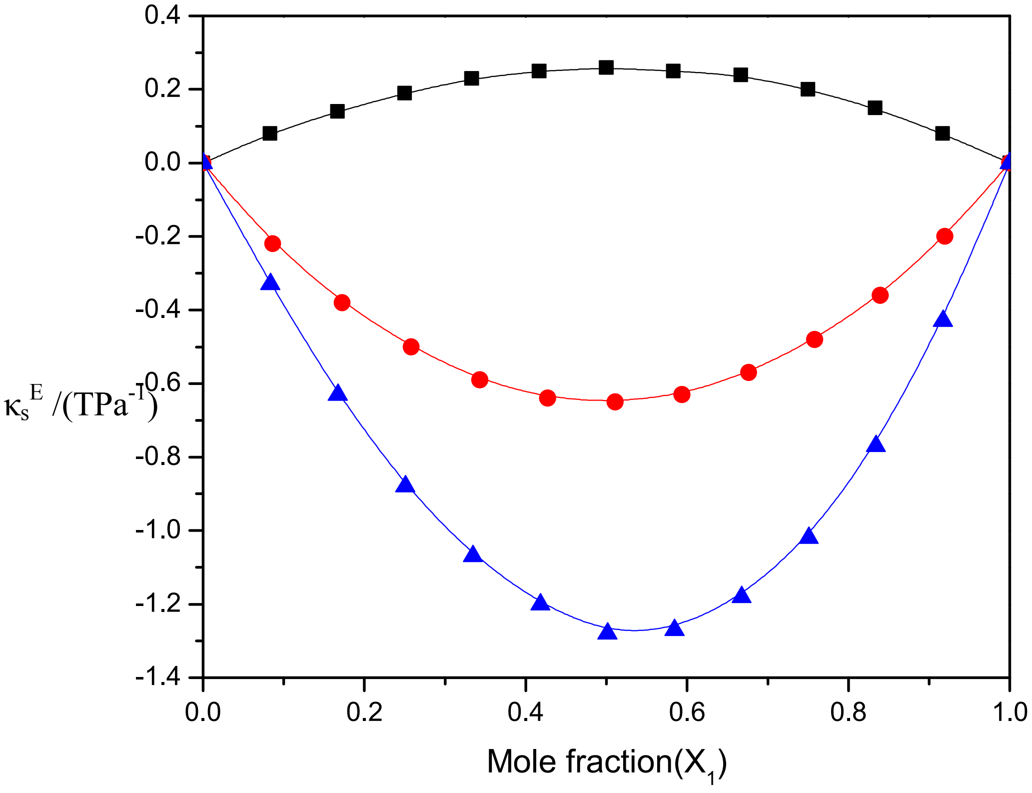

Figure4

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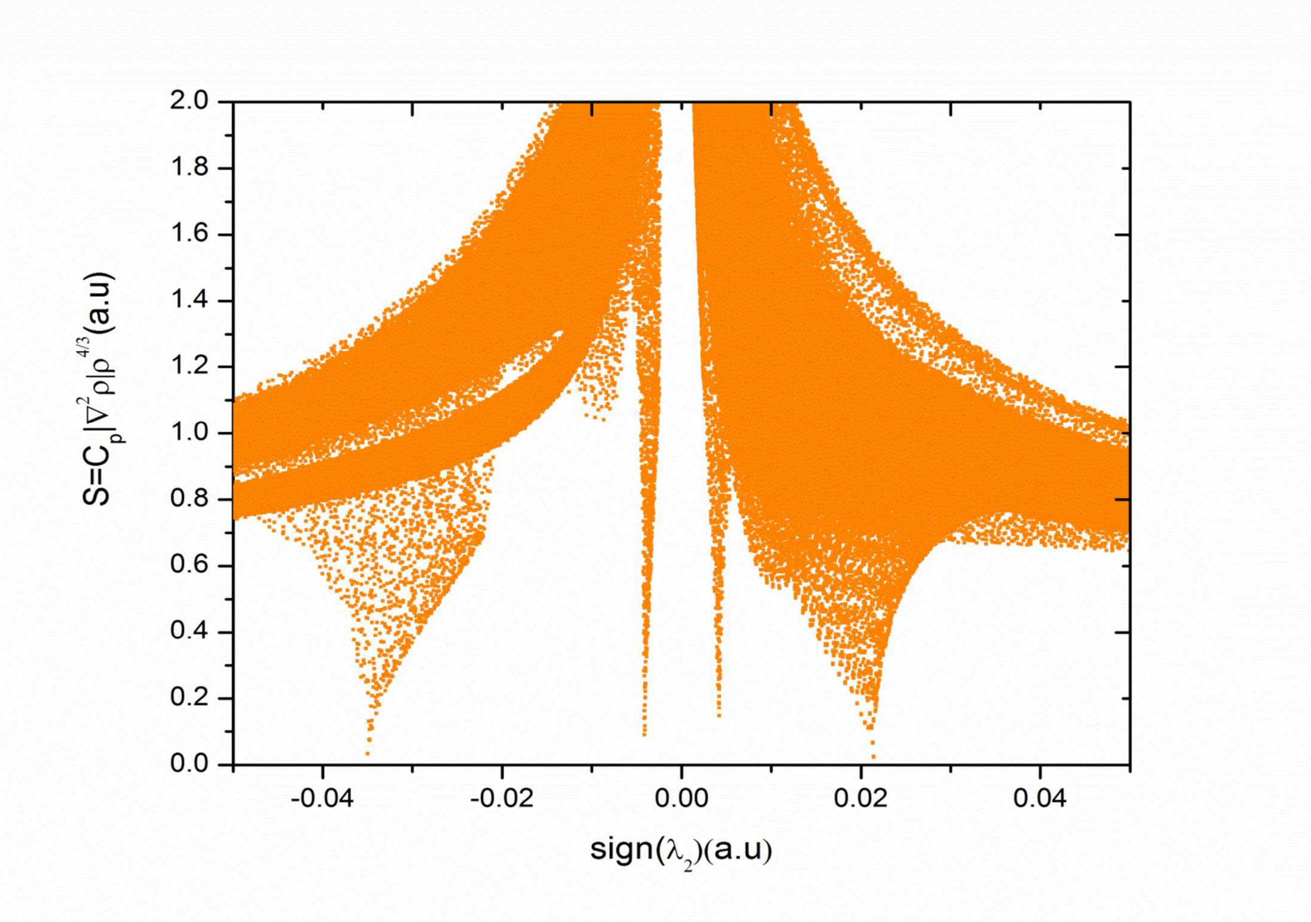

Figure 5(a1)

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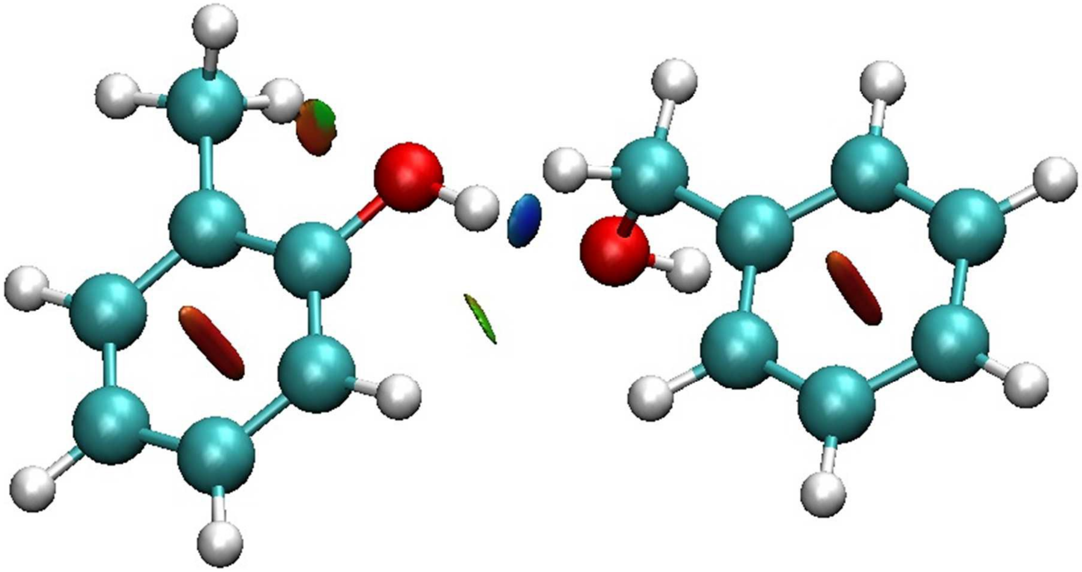

Figure 5(a2)

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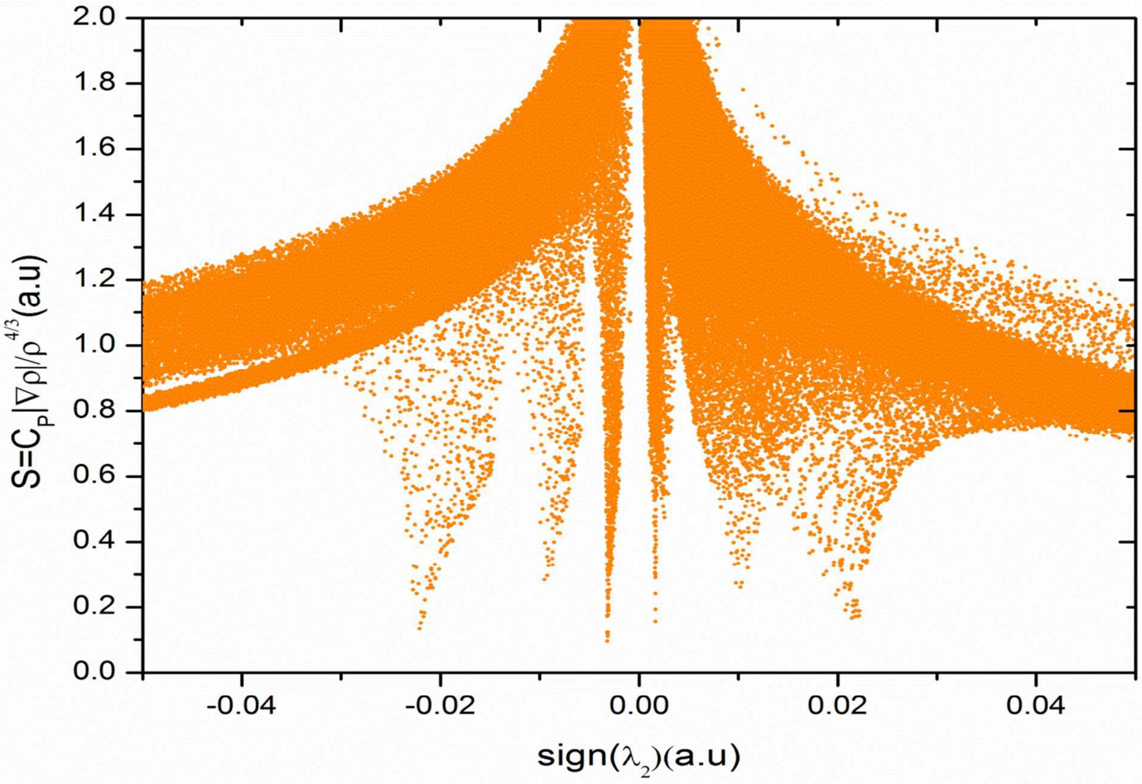

Figure 5(b1)

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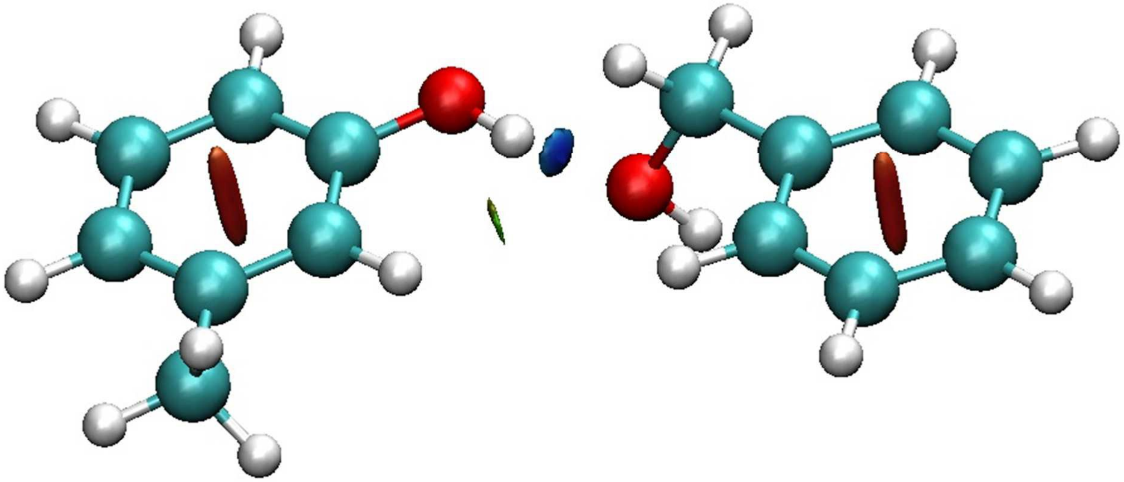

Figure 5(b2)

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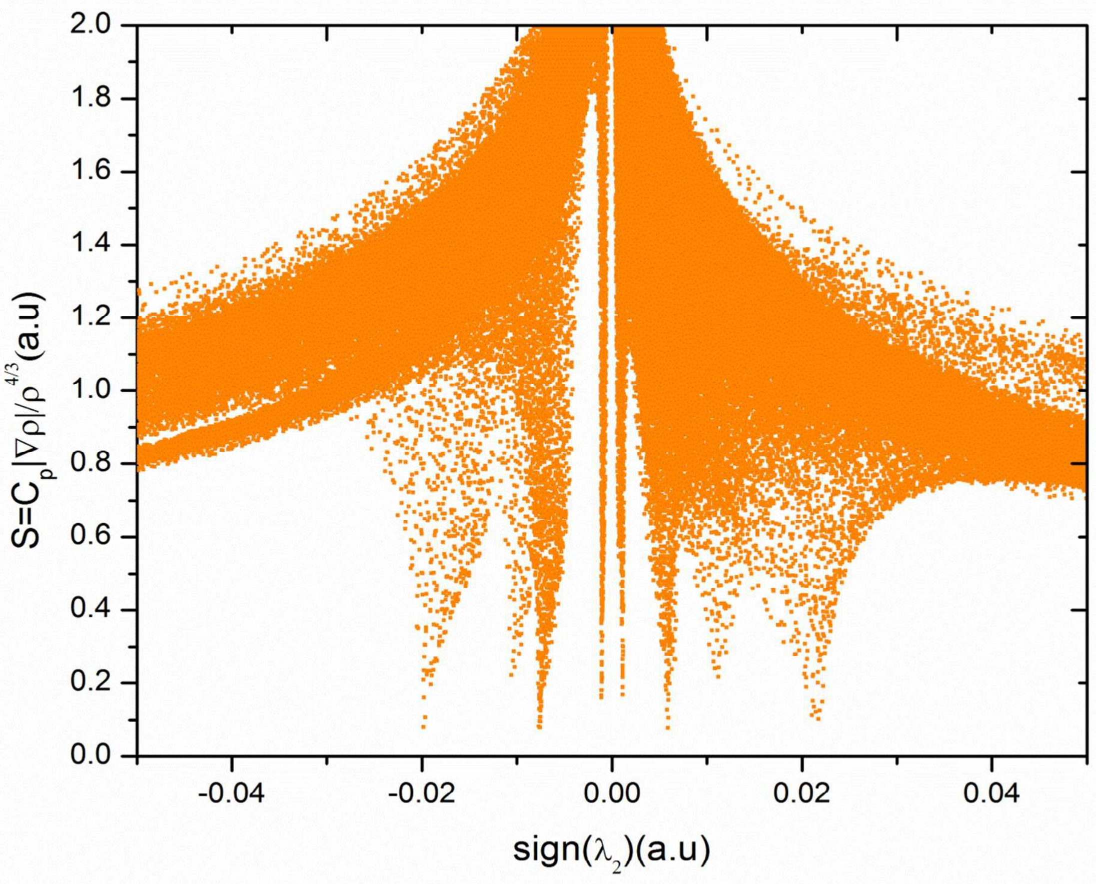

Figure 5(c1)

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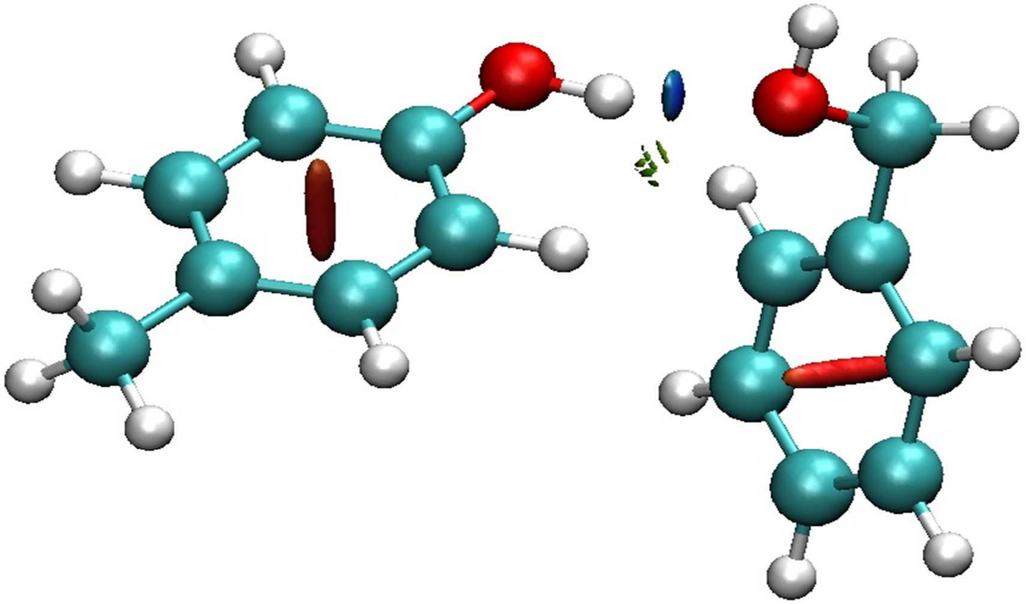

Figure 5(c2)

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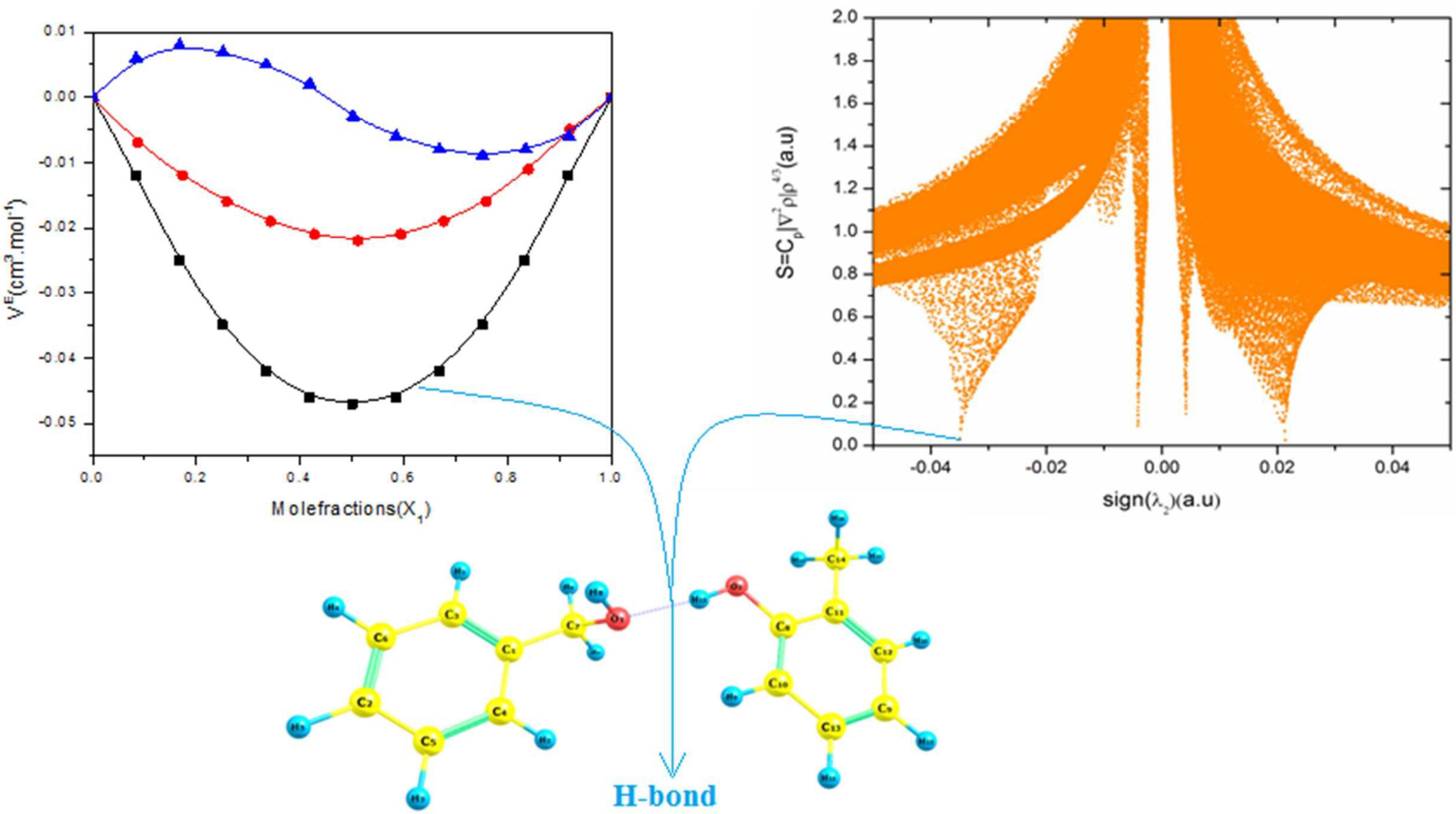

The effect of hydrogen bonding on excess volumes: The graphical representation of excess volume and reduced density gradient scattered plot of benzylalcohol with *o*-cresol.

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