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Thermophysical, acoustical, spectral and DFT study of intermolecular interactions of terpinolene with cresols

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Densities and speed of sound have been measured experimentally for binary mixtures of terpinolene with cresols (o-cresol, m-cresol, p-cresol) at three different temperatures 303.15, 308.15 and 313.15 K at atmospheric pressure. From primary physical properties, some secondary properties like molar volume (V_m), excess molar volume (V_m^E), partial molar volume $(\bar{V}^{o}_{m,i})$, excess partial molar volume $(\bar{V}^{o,E}_{m,i})$, apparent molar volume $(V_{m,\Phi,i})$, deviation in speed of sound (Δu), isentropic compressibility (κ_s), deviation in isentropic compressibility $(\Delta\kappa_s)$, acoustical impedance (z), deviation in acoustical impedances (Δz), intermolecular free length (L_f), partial molar isentropic compression$(\bar{K}^{o}_{s,m,i})$, excess partial molar isentropic compression$(\bar{K}^{o,E}_{s,m,i})$ and apparent molar isentropic compression$(K_{s,m,\Phi,i})$ have been calculated. Infinite dilution apparent molar volume $(V^{o}_{m,\Phi,1})$, infinite dilution apparent molar isentropic compression$(K^{o}_{s,m,\Phi,1})$, empirical parameters S_v, B_v and S_k, B_k of the Redlich-Rosenberg-Mayer equation with the limiting apparent molar expansibility(E^{o}_{Φ}) have been also calculated along with some theoretical speed of sound calculating relations such as Nomoto relation (u_{nmt}), Ideal mixture relation (u_{imr}), Junji relation (u_{junji}) and Free length theory relation (u_{flt}) with their standard deviation (σ). All the calculated values of excess/deviation properties have been fitted with the fourth order Redlich-Kister polynomial equation and their standard deviation (σ) values are also calculated. FTIR spectral analysis of binary mixtures at 4:1, 1:1 and 1:4 composition ratios have been carried out at 298.15 K. Computational calculations such as optimization of pure and binary mixtures in gas phase, bond length, Mulliken charges, theoretical vibrational frequencies and NBO calculations on basis of the DFT (Density Functional Theory) have been also carried out. The results are discussed in term of presence of intermolecular interactions, types, strength and behavior with change of temperatures and cresol components in binary mixtures.

Keywords: Densities, Speed of sound, Deviation properties, FT-IR analysis, DFT, Binary mixtures

The study of thermophysical properties plays a significant role to understand the presence of intermolecular interactions in liquid mixtures as we know that intermolecular interactions play a vital role in many physical techniques such as extraction, separation and also in many sophisticated analytical techniques such as HPLC, HPTLC etc. Terpinolene is used in many products of day to day use because of its taste, odour and pharmaceutical applications[1,2]. This kind of combined study using thermophysical, spectral and computational calculations give us the information about the behavior of terpinolene molecules in different solvents' environment. As we know that the intermolecular interactions depend upon the properties of the functional groups of solvent, the study of thermophysical properties in combination with spectral and quantum computational calculations make better interpretation as well as understanding of types of interactions such as electrostatic, non-electrostatic and hydrogen bonding etc. So in this work, we have selected cresol (o-cresol, m-cresol, p-cresol) components as a second component of binary mixtures because cresol molecules contains $-OH$ (hydroxyl), $-CH_3$ (methyl) and also aromatic ring. Studies of thermophysical data by changing cresol molecules from o-cresol to p-cresol, also gives an information that how different substitution position of cresol molecules affect the intermolecular interactions with terpinolene component in the mixture.

Materials and Methods

All chemicals of AR grade were used for this present study and were used after purification using standard methods[3,4]. Furthermore, details about its suppliers were as per given in Table 1. The comparison of experiment and literature values of densities and speed of sound were given in form of Table 2 and the data of this table shows very close proximity.

Table 1 — List of chemicals with details of supplier, CAS number, purity, purification method and applied method for final purity analysis

Compound/ Grade	Supplier	CAS number	Initial mass-fraction purity	Purification method	Final mass-fraction purity	Analysis method
Terpineol	Sigma-Aldrich Chemical,USA	586-62-9	90%	None	-	-
o-cresol	S.D.Fine Chemicals Ltd.	95-48-7	99%	Fractional distillation	99.5%	GC[a]
m-cresol	S.D.Fine Chemicals Ltd.	108-39-4	99%	Fractional distillation	99.5%	GC[a]
p-cresol	S.D.Fine Chemicals Ltd.	106-44-5	99.%	Fractional distillation	99.5%	GC[a]

[a] GC = Gas-liquid chromatography

Table 2 — Experimental and literature values of density (ρ) and speed of sound ($\boldsymbol{u}$)of pure components at 303.15, 308.15 and 313.15 K

Pure compound	T/K	ρ /(g·cm^3)		u /(m·s^{-1})	
		Exp.	Lit.	Exp.	Lit.
Terpinolene	303.15	0.853890	-----	1350.48	----
	308.15	0.849991	-----	1330.99	----
	313.15	0.846075	-----	1311.33	----
o-Cresol	303.15	1.037029	1.0369[30] 1.0487[31]	1487.70	1487[30]
	308.15	1.032655	1.0316[30] 1.03273[32]	1470.56	1478[37] 1470[30]
	313.15	1.028261	1.0260[33] 1.0391[32]	1453.38	1462[31]
m-Cresol	303.15	1.026135	1.0261[34]	1465.61	1465[30]
	308.15	1.022187	1.02164[35]	1449.94	1450[30]
	313.15	1.018215	1.0160[33]	1434.28	-----
p-Cresol	303.15	1.025991	1.0263[30]	1472.23	1471[30]
	308.15	1.022115	1.02198[36] 1.0224[30]	1456.73	1455[30]
	313.15	1.018204	1.0168[33] 1.01805[36]	1441.02	-----

Standard uncertainties $\boldsymbol{u}$, in case of $\boldsymbol{\rho}$ and $\boldsymbol{uu(T)}$ = ±0.001 K and the combined expanded uncertainty$\boldsymbol{U_C}$ is $\boldsymbol{U_C(\rho)}$ = ±0.000001 g·cm^3 and $\boldsymbol{U_C(u)}$ = ±0.1 m·s^{-1} with 0.95 level of confidence ($\boldsymbol{k \approx 2}$). All physical quantities are measured at atmospheric pressure

Apparatus and procedure

Sample preparation

All the binary liquid mixtures were prepared by mixing their appropriate amount using electronic balance (Reptech RA–2012) having accuracy in measurement of weight ±0.0001 g. All the binary mixtures were prepared in airtight ground glass ampoules to avoid losses of components due to evaporation phenomena and were kept in dark place to avoid photolytic effect.

Measurement of density ($\boldsymbol{\rho}$) and speed of sound($\boldsymbol{u}$)

Density and speed of sound values for pure components and their binary mixtures were measured using an automatic density and speed of sound measuring meter (Model: DSA 5000 M, Anton Paar, India) with measuring accuracy ±0.000005 g·cm^{-1} for density and ±0.1 m·s^{-1} for speed of sound. During the measurement, the temperature was maintained by inbuilt temperature controlling system with accuracy of ±0.001 °C (0.002 °F). The instrument was calibrated by highly pure deionized water supplied by manufacturer.

FTIR spectra measurement

FTIR spectra of pure components and their binary mixtures were recorded by alpha – FTIR spectrometer (Bruker, Germany) with 2 cm^{-1} of resolution and 4 scan rate at 298.15 K. The Spectra were recorded at 4:1, 1:1 and 1:4 (v/v %) composition ratios. The FTIR spectra were corrected for the water vapour and CO_2 contributions.

Quantum computational calculations

The geometrical optimization, vibrational and energy calculations including NBO analysis for pure components, their binary mixtures in gas phase 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) basis set. The completion of optimized structures was confirmed by checking the absence of the imaginary frequency in vibrational calculations. All quantum computational calculations were performed using Gaussian 16[5] and their visualization of all Gaussian calculations were carried out using Gauss View 6[6].

Results and Discussion

Density (ρ)and excess molar volume (V_m^E)

The experimentally measured values of density (ρ) and calculated values of excess molar volume (V_m^E) for binary mixtures at 303.15, 308.15 and 313.15 K over entire composition range are listed in Table 3. Graphical representation of (V_m^E) vs. mole fraction

Table 3 — Density (ρ) and excess molar volume (V_m^E) vs mole fraction (x_1) for Terpinolene + o-, m-, and p-Cresol mixtures at different temperatures

x_1		ρ (g·cm^3)			V_m^E (cm^3·mol^{-1})	
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
Terpinolene (1) + o-Cresol (2)						
0.0000	1.037029	1.032655	1.028261	0.0000	0.0000	0.0000
0.0677	1.019331	1.014881	1.010434	-0.0653	-0.0532	-0.0435
0.1404	1.001488	0.997051	0.992583	-0.1216	-0.1060	-0.0888
0.2188	0.983525	0.979095	0.974682	-0.1701	-0.1495	-0.1329
0.3035	0.965436	0.961057	0.956698	-0.2085	-0.1876	-0.1713
0.3953	0.947226	0.942921	0.938634	-0.2352	-0.2168	-0.2031
0.4950	0.928884	0.924644	0.920409	-0.2464	-0.2292	-0.2151
0.6040	0.910381	0.906192	0.902005	-0.2343	-0.2159	-0.2004
0.7233	0.891733	0.887586	0.883458	-0.1966	-0.1751	-0.1592
0.8547	0.872911	0.868847	0.864801	-0.1227	-0.1043	-0.0918
1.0000	0.853890	0.849991	0.846075	0.0000	0.0000	0.0000
Terpinolene (1) + m-Cresol (2)						
0.0000	1.026135	1.022187	1.018215	0.0000	0.0000	0.0000
0.0684	1.009415	1.005379	1.001334	-0.0545	-0.0461	-0.0390
0.1417	0.992572	0.988521	0.984458	-0.1009	-0.0911	-0.0823
0.2206	0.975649	0.971601	0.967515	-0.1428	-0.1332	-0.1216
0.3057	0.958614	0.954564	0.950497	-0.1752	-0.1649	-0.1549
0.3978	0.941462	0.937442	0.933392	-0.1954	-0.1882	-0.1796
0.4977	0.924217	0.920196	0.916159	-0.2046	-0.1959	-0.1876
0.6065	0.906817	0.902814	0.898796	-0.1911	-0.1830	-0.1755
0.7254	0.889317	0.885328	0.881323	-0.1591	-0.1506	-0.1424
0.8560	0.871671	0.867702	0.863726	-0.0969	-0.0883	-0.0814
1.0000	0.853890	0.849991	0.846075	0.0000	0.0000	0.0000
Terpinolene (1) + p-Cresol (2)						
0.0000	1.025991	1.022115	1.018204	0.0000	0.0000	0.0000
0.0684	1.009142	1.005191	1.001249	-0.0390	-0.0346	-0.0310
0.1417	0.992253	0.988257	0.984315	-0.0777	-0.0714	-0.0672
0.2207	0.975286	0.971270	0.967318	-0.1113	-0.1054	-0.0990
0.3058	0.958238	0.954204	0.950258	-0.1384	-0.1327	-0.1256
0.3978	0.941094	0.937042	0.933118	-0.1556	-0.1497	-0.1435
0.4977	0.923846	0.919783	0.915881	-0.1598	-0.1540	-0.1486
0.6065	0.906467	0.902394	0.898519	-0.1444	-0.1382	-0.1338
0.7255	0.889001	0.884912	0.881054	-0.1124	-0.1042	-0.0988
0.8560	0.871448	0.867369	0.863548	-0.0606	-0.0539	-0.0504
1.0000	0.853890	0.849851	0.846075	0.0000	0.0000	0.0000

Standard uncertainties $\boldsymbol{u}$ are $\boldsymbol{u(T)}$ = ±0.001 K, $\boldsymbol{u(x_1)}$ = ±0.0001, and the combined expanded uncertainty $\boldsymbol{U_C}$ is $\boldsymbol{U_C(\rho)}$ = ±0.000001 g·cm^3 with 0.95 level of confidence ($\boldsymbol{k \approx 2}$). All physical quantities are measured at atmospheric pressure

(x_1) at 303.15 K is shown as Fig. S1 (Supplementary Data). Excess molar volume (V_m^E) is calculated using following equations.

$$V_m^E(cm^3.mol^{-1}) = V_m - V_1x_1 - V_2x_2 \qquad ...(1)$$

$$V_m^E(cm^3.mol^{-1}) = \left(\frac{x_1M_1+x_2M_2}{\rho_m}\right) - \left(\frac{x_1M_1}{\rho_1}\right) - \left(\frac{x_2M_2}{\rho_2}\right) \qquad ...(2)$$

where, V_m, V_i represents the molar volumes of mixture and ith component. x_i, M_i represents the mole fraction and molar masses of ith component. ρ_m,ρ_i represents densities of a binary liquid mixture and ith component.

Some observations that are made from the values of (V_m^E) in Table 3 are as under.

1. Excess molar volume (V_m^E) values for all binary mixtures are negative at all studied temperatures.
2. The negative value of V_m^E decreases with increase of temperature.
3. The (terpinolene + o-cresol) binary mixture show the highest negative values of (V_m^E) amongst all binary mixtures.

V_m^E values are affected by major two factors as we briefly discussed in our earlier research article[1]. From that discussion, negative value of V_m^E are due to the presence of strong intermolecular interactions between unlike molecules and positive value of V_m^E results of the presence of weak attractive or repulsive type interactions between components of binary mixtures[7-11].

A perusal of Table 3 shows that the o-cresol molecules show the highest strong interaction with terpinolene molecules. The interactions decrease with rise of temperature. This trend can be understood by the fact that at a higher temperature, the molecules get more kinetic energy. Due to higher energy the strength of hydrogen bonding or electrostatic type interaction decreases. So the molecules orient at some large distance from each other. The interaction order of cresols with terpinolene follows the order: o-cresol>m-cresol>p-cresol.

Infinite dilution partial molar volume ($\bar{V}^o_{m,i}$), excess partial molar volume ($\bar{V}^{o,E}_{m,i}$) and apparent molar volume ($V_{m,\Phi,i}$)

The calculated values of infinite dilution partial molar volume ($\bar{V}^o_{m,i}$), excess partial molar volume ($\bar{V}^{o,E}_{m,i}$), apparent molar volume ($V_{m,\Phi,i}$) are listed in Table S1. The graphical representation of these properties is shown as Fig. 1, 2 and S2-S7 (Supplementary Data).$\bar{V}^o_{m,i}$, $\bar{V}^{o,E}_{m,i}$, $V_{m,\Phi,i}$ were calculated using following standard equations[12].

$$\bar{V}^o_{m,1} = V_m^E + V^*_{m,1} + x_2\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P} \qquad ...(3)$$

$$\bar{V}^o_{m,2} = V_m^E + V^*_{m,2} - x_1\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P} \qquad ...(4)$$

where, V_m^E, $V^*_{m,i}$ and $\bar{V}^o_{m,i}$ represent the excess molar volume of mixture, molar volume and partial molar volume of ith component, respectively. Taking

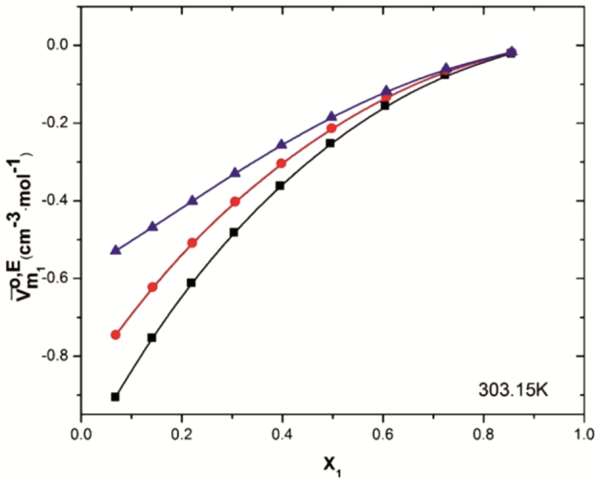

Fig. 1 — Infinite Dilution excess partial molar volume ($\bar{V}^{o,E}_{m_1}$)for the system Terpinolene (1) + o-, m-, and p-cresol (2) as a function of mole fraction at T = 303.15 K: ■, Terpinolene (1) + o-cresol (2); ●, Terpinolene (1) + m-cresol (2); ▲, Terpinolene (1) + p-cresol (2).

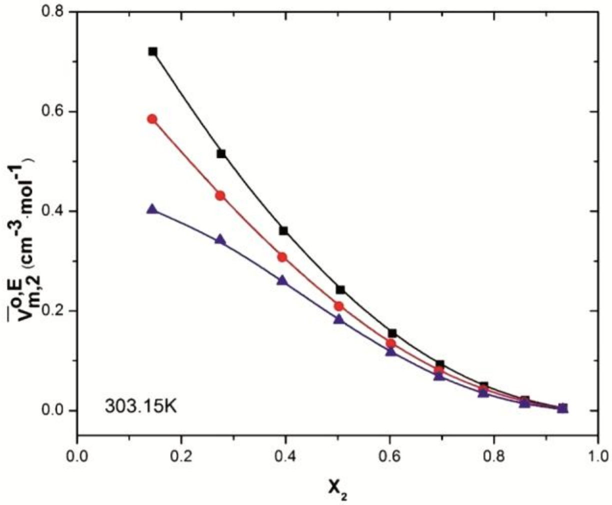

Fig. 2 — Infinite dilution excess partial molar volume ($\bar{V}^{o,E}_{m_2}$)for the system Terpinolene (1) + o-, m-, and p-cresol (2) as a function of mole fraction at T = 303.15 K: ■, Terpinolene (1) + o-cresol (2); ●, Terpinolene (1) + m-cresol (2); ▲, Terpinolene (1) + p-cresol (2).

differentiation of $\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P}$ derivative, we get the following relations.

$$\bar{V}^{o}_{m,1}=V^{*}_{m,1}+x_2^2\sum_{i=0}^{n}A_i(1\text{-}2x_1)^{i}-2x_1x_2^2\sum_{i=1}^{n}A_i(1\text{-}2x_1)^{i-1} \quad \ldots(5)$$

$$\bar{V}^{o}_{m,2}=V^{*}_{m,2}+x_1^2\sum_{i=0}^{n}A_i(1\text{-}2x_1)^{i}+2x_1^2x_2\sum_{i=1}^{n}A_i(1\text{-}2x_1)^{i-1} \quad \ldots(6)$$

The excess partial molar volume of binary mixtures was calculated using following relation.

$$\bar{V}^{o,E}_{m,1}\ (cm^3.mol^{-1})=\bar{V}^{o}_{m,1}-V^{*}_{m,1} \quad \ldots(7)$$

$$\bar{V}^{o,E}_{m,2}\ (cm^3.mol^{-1})=\bar{V}^{o}_{m,2}-V^{*}_{m,2} \quad \ldots(8)$$

where, $\bar{V}^{o}_{m,i}$ represent the partial molar volume of ith component.

Some observations made from the values of infinite dilution partial molar volume ($\bar{V}^{o}_{m,i}$) and excess partial molar volume ($\bar{V}^{o,E}_{m,i}$) are as follows.

1. All the binary mixtures show the negative values of $\bar{V}^{o,E}_{m,1}$.
2. (Terpinolene + o-cresol) binary mixture shows the highest negative value of $\bar{V}^{o,E}_{m,1}$ and the lowest negative value of $\bar{V}^{o,E}_{m,1}$ is observed in p-cresol containing binary mixture.

The o-cresol molecules are strongly attracted to terpinolene molecules by intermolecular interactions and hence the highest negative value of $\bar{V}^{o,E}_{m,1}$. The strength of intermolecular interactions is decreasing with rise of temperature due to increase in kinetic energy of molecules which results in the less negative value of $\bar{V}^{o,E}_{m,1}$ at higher temperature.

Apparent molar volume values have been calculated using following two different relations.

Method 1*[13]*.

$$V_{m,\phi,i}\ (cm^3.mol^{-1})=\frac{M}{\rho}-\frac{(\rho-\rho_o)}{m\rho\,\rho_o} \quad \ldots(9)$$

where, M, m represents the molar mass and molality of solute molecules and ρ, ρ_o represents the density of mixture and solute molecules, respectively.

Method 2.

$$V'_{m,\phi,1}\ (cm^3.mol^{-1})=\left(\frac{V_m-(1-x_1)\bar{V}^{o}_{m,2}}{x_1}\right) \quad \ldots(10)$$

$$V'_{m,\phi,2}\ (cm^3.mol^{-1})=\left(\frac{V_m-x_1\bar{V}^{o}_{m,1}}{(1-x_1)}\right) \quad \ldots(11)$$

Using the equation of V_m^E in above equations, we get

$$V'_{m,\phi,1}(cm^3.mol^{-1})=\bar{V}^{o}_{m,1}+\left(\frac{V_m^E}{x_1}\right) \quad \ldots(12)$$

$$V'_{m,\phi,2}(cm^3.mol^{-1})=\bar{V}^{o}_{m,2}+\left(\frac{V_m^E}{x_2}\right) \quad \ldots(13)$$

where, $V'_{m,\phi,i}$, represents the apparent molar volume of ith component.

Infinite dilution apparent molar volume $V^{o}_{m,\Phi,1}$ for all binary mixtures were calculated using following shown the Redlich-Rosenberg-Mayer relation[13].

$$V_{m,\phi,1}=V^{o}_{m,\phi,1}+S_v m^{1/2}+B_v m \quad \ldots(14)$$

where, S_v and $B_v$represents empirical parameters.

The limiting apparent molar expansibility (E^{o}_{Φ}) for all binary mixtures were calculated using following relations[13].Values of empirical parameters S_v, B_v and the limiting apparent molar expansibility(E^{o}_{Φ}) are given in Table S3 (Supplementary Data).

Temperature dependence for $V^{o}_{m,\phi,i}$were calculated using following relation.

$$V^{o}_{m,\phi,i}=A+BT+CT^2 \quad \ldots(15)$$

The limiting apparent molar expansibility (E^{o}_{Φ}) were calculated by differentiation of the above equation with respect to temperature (T).

$$E^{o}_{\Phi}=\left(\frac{\partial V^{o}_{\Phi}}{\partial T}\right)=B+2CT \quad \ldots(16)$$

Where, A, B and Crepresents temperature dependence constants of $V^{o}_{m,\phi,i}$.

The $V^{o}_{m,\Phi,1}$ values are increasing with increase of temperature that indicates the weakening of intermolecular interactions between binary mixture components at a higher temperature. At 303.15 K, the lowest positive value is observed for o-cresol containing binary mixture and the highest positive value is observed for p-cresol containing binary mixture indicating that the o-cresol molecules show the strongest intermolecular interaction with terpinolene molecules. The empirical parameter S_v possesses the positive and B_v possesses the negative value for all binary mixtures that also gives information regarding presence of intermolecular interactions between charged atoms of components of binary mixtures[14]. These values also support the interaction order given from V_m^E values.

Speed of Sound (u) and deviation in speed of sound (Δu)

The values of speed of sound (u) and deviation in speed of sound (Δu) over the entire composition range for all binary mixtures at all studied temperatures are listed in Table 4. The graphical representation of Δu vs. mole fraction (x_1) at 303.15 K is shown as Fig. S8 (Supplementary Data). Deviation in the speed of sound (Δu) was calculated using the following relation.

$$\Delta u\ (m\cdot s^{-1}) = u_{exp} - (x_1 u_1 + x_2 u_2) \qquad \ldots(17)$$

where, u_{exp}, x_i, u_i represents speed of sound of mixture, mole fraction and speed of sound of ith pure component, respectively. The values of Table 4 reveals that all the binary mixtures show the positive Δu values at all studied temperatures, the positive Δu values decrease with increase of temperature and the highest Δu values are observed for o-cresol containing binary mixture.

Table 4 — Speed of sound (u) and deviation in speed of sound (Δu) vs mole fraction (x_1) for Terpinolene + o-, m- and p-Cresol mixtures at 303.15, 308.15 and 313.15 K

x_1	u (m·s^{-1})			Δu (m·s^{-1})		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
Terpinolene (1) + o-Cresol (2)						
0.0000	1487.70	1470.56	1453.38	0.00	0.00	0.00
0.0677	1479.48	1461.89	1444.32	1.07	0.78	0.56
0.1404	1471.37	1453.28	1435.27	2.94	2.32	1.84
0.2188	1462.78	1444.23	1425.94	5.11	4.21	3.64
0.3035	1453.31	1434.41	1415.78	7.25	6.21	5.51
0.3953	1442.31	1423.12	1404.15	8.85	7.73	6.92
0.4950	1429.19	1409.85	1390.61	9.42	8.38	7.55
0.6040	1413.42	1393.78	1374.29	8.60	7.52	6.70
0.7233	1394.50	1374.82	1355.19	6.05	5.21	4.56
0.8547	1372.87	1353.29	1333.63	2.45	2.02	1.66
1.0000	1350.48	1330.99	1311.33	0.00	0.00	0.00
Terpinolene (1) + m-Cresol (2)						
0.0000	1465.61	1449.94	1434.28	0.00	0.00	0.00
0.0684	1458.48	1442.39	1426.28	0.74	0.58	0.41
0.1417	1451.45	1434.85	1418.29	2.16	1.77	1.44
0.2206	1444.05	1426.92	1409.98	3.84	3.22	2.83
0.3057	1435.89	1418.45	1401.02	5.48	4.88	4.33
0.3978	1426.65	1408.81	1390.94	6.84	6.19	5.57
0.4977	1415.65	1397.45	1379.22	7.34	6.71	6.13
0.6065	1402.35	1383.76	1365.15	6.57	5.96	5.44
0.7254	1386.68	1367.74	1348.75	4.59	4.09	3.66
0.8560	1368.95	1349.73	1330.39	1.89	1.61	1.36
1.0000	1350.48	1330.99	1311.33	0.00	0.00	0.00
Terpinolene (1) + p-Cresol (2)						
0.0000	1472.23	1456.73	1441.02	0.00	0.00	0.00
0.0684	1464.33	1448.40	1432.29	0.43	0.27	0.14
0.1417	1456.38	1440.01	1423.55	1.41	1.10	0.91
0.2207	1448.23	1431.44	1414.58	2.86	2.45	2.18
0.3058	1439.45	1422.25	1404.92	4.45	3.97	3.55
0.3978	1429.38	1411.78	1394.15	5.58	5.07	4.72
0.4977	1417.73	1399.81	1381.71	6.10	5.66	5.24
0.6065	1403.87	1385.52	1367.02	5.48	5.05	4.66
0.7255	1387.75	1368.92	1350.01	3.84	3.41	3.08
0.8560	1369.49	1350.31	1331.00	1.48	1.22	1.00
1.0000	1350.48	1330.99	1311.33	0.00	0.00	0.00

Standard uncertainties u are $u(T)$ = ±0.001 K, $u(x_1)$ = ±0.0001, and the combined expanded uncertainty U_C is $U_C(u)$ = ±0.1 m·s^{-1} with 0.95 level of confidence ($k \approx 2$). All physical quantities are measured at atmospheric pressure

The positive Δu values results when molecules try to orient tightly or closely to each other in liquid mixture and this condition facitates sound wave to pass through the molecules and results in high value of speed of sound (u). So positive value of Δu indicates the present of strong intermolecular interactions such as electrostatic or hydrogen bonding type. Negative values of Δu show weak intermolecular interaction between components of binary mixture[15,16]. From the values of Δu of Table 4, we can say that the o-cresol molecules show the strongest intermolecular interactions with terpinolene molecules and the strength of interactions decrease with increase of temperature[15,16].

Theoretical Speed of Sound Relations

The average percentage deviation (σ%) values of various theoretical speed of sound relations such as Nomoto relation (u_{nmt}), ideal mixture relation (u_{imr}), Junji relation (u_{junji}) and Free length theory relation (u_{flt}) are given in Table 5. Their standard equations are as given follows.

I. Junjie equation[17]

$$\mathrm{u_{junji}}=\left\{\left(\frac{\mathrm{x_1M_1}}{\rho_1}\right)+\left(\frac{\mathrm{x_2M_2}}{\rho_2}\right)\right\}/\left\{(\mathrm{x_1M_1+x_2M_2})^{\frac{1}{2}}\left[\left(\frac{\mathrm{x_1V_1}}{\rho_1\mathrm{u_1^2}}\right)+\left(\frac{\mathrm{x_2V_2}}{\rho_2\mathrm{u_2^2}}\right)^{1/2}\right]\right\} \quad ...(18)$$

Table 5 — Average percentage deviation (σ%) in the speed of sound from various theoretical relations for Terpinolene + o-, m- and p-Cresol mixtures at 303.15, 308.15 and 313.15 K.

Theoretical Relations	T (K)		
	303.15	308.15	313.15
Terpinolene (1) + o-Cresol (2)			
u_{nmt}	1.21706	1.19178	1.18209
u_{imr}	0.75349	0.70511	6.10207
u_{junji}	2.07803	2.07670	1.89897
u_{flt}	2.62964	2.63971	2.64427
Terpinolene (1) + m-Cresol (2)			
u_{nmt}	0.97684	0.97936	0.98773
u_{imr}	0.64765	0.61864	0.59410
u_{junji}	1.68391	1.71511	1.56735
u_{flt}	1.89233	1.95167	2.01189
Terpinolene (1) + p-Cresol (2)			
u_{nmt}	0.95322	0.96531	0.98237
u_{imr}	0.58807	0.56766	0.55254
u_{junji}	1.68997	1.73372	1.78225
u_{flt}	2.24705	2.27564	2.30127

nmt = Nomoto, imr = Ideal mixture relation, junji= junji ,flt = Free length Theory

where, x_i, M_i, ρ_i and u_i represents mole fraction, molar mass, density and speed of sound of i^th pure component, respectively.

II. Nomoto equation[18]

$$u_{nom}=\left\{\frac{x_1R_1+x_2R_2}{x_1V_1+x_2V_2}\right\}^3 \quad ...(19)$$

where, V_i represnts molar volume of i^th pure component. R_i is Wada's constant and were calculated using following relation

$$R_i = u_i^{1/3}V_i \quad ...(20)$$

where, u_i represents speed of sound of i^th component.

III. Ideal mixture relation[19]

$$\mathrm{u_{imr}}=[1/(\mathrm{x_1M_1+x_2M_2})^{1/2}]\left\{1/\left[\left(\frac{\mathrm{x_1}}{\mathrm{M_1u_1^2}}\right)+\left(\frac{\mathrm{x_2}}{\mathrm{M_2u_2^2}}\right)\right]^{1/2}\right\} \quad ...(21)$$

where, M_i, and u_i, represents molar mass and sound velocities of i^th component, respectively.

IV. Free length theory[20]

$$u_{flt} = \{[x_1(V_{M1}-V_{0.1})u_1\rho_1^{1/2}]+[x_2(V_{M2}- V0.2u2\rho21/2/[VM-x1V0.1+x2V0.2]\rho1/2 \quad ...(22)$$

where, ρ, V_M, x_1, V_{M_i} represent density, molar volume of mixture, mole fraction and molar volume of i^th component, respectively.

From Table 5, it is observed that the Ideal mixture relation (u_{imr}) shows the lowest σ% values for all binary mixtures at all studied temperatures except for terpinolene + o-cresol binary mixture at 313.15 (Junji relation (u_{junji})). The Free length theory (u_{flt}) relation shows the highest σ% values for all binary mixtures at all studied temperatures except for terpinolene + o-cresol at 313.15 K (Ideal mixture relation (u_{imr}))

Isentropic compressibility (κ_s), deviation in isentropic compressibility ($\Delta\kappa_s$), acoustical impedance (z), deviation in acoustical impedance (Δz) and intermolecular free length (L_f)

The calculated values of isentropic compressibility (κ_s), deviation in isentropic compressibility ($\Delta\kappa_s$), acoustical impedance (z), deviation in acoustical impedances (Δz) and intermolecular free length (L_f) for all binary mixtures over the entire composition range at all studied temperatures are given in Table S7 to S9 (Supplementary Data), respectively. The graphical representation of $\Delta\kappa_s$ and Δz vs. mole fraction (x_1) is shown as Fig. 3 and 4, respectively.

These properties were calculated using following relations[21].

$$\kappa_s (T\,Pa^{-1}) = \frac{1}{u_i^2 \rho_i} \qquad \ldots(23)$$

$$Z\,(g \cdot m^{-2} \cdot s^{-1}) = u_i \rho_i \qquad \ldots(24)$$

$$Lf = K \kappa_s^{1/2} \qquad \ldots(25)$$

$$\Delta\kappa_s = \kappa_{s_{exp}} - \left(x_1 \kappa_{s_1} + x_2 \kappa_{s_2}\right) \qquad \ldots(26)$$

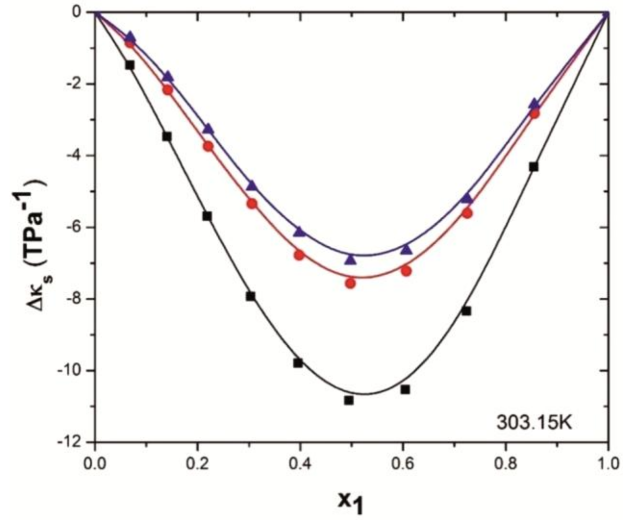

Fig. 3 — Deviation in isentropic compressibility (Δk_s) for the system Terpinolene (1) + o-, m-, and p-cresol (2) as a function of mole fraction at T = 303.15 K: ■, Terpinolene (1) + o-cresol (2); ●, Terpinolene (1) + m-cresol (2); ▲, Terpinolene (1) + p-cresol (2).

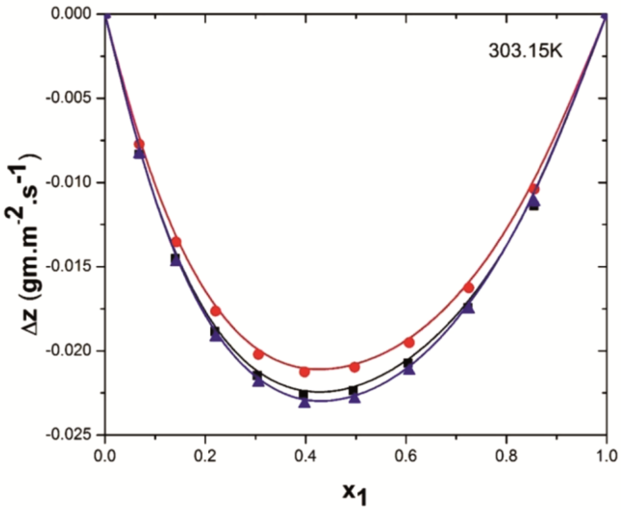

Fig. 4 — Deviation in acoustical impedance (Δz) for the system Terpinolene (1) + o-, m-, and p-cresol (2) as a function of mole fraction at T = 303.15 K: ■, Terpinolene (1) + o-cresol (2); ●, Terpinolene (1) + m-cresol (2); ▲, Terpinolene (1) + p-cresol (2).

$$\Delta z = z_{exp} - (x_1 z_1 + x_2 z_2) \qquad \ldots(27)$$

where, u_i, ρ_i,x_i,ϕ_i, κ_{s_i} and z_i represent speed of sound, density mole fraction, volume fraction, isentropic compressibility and acoustical impedance of i^th component, respectively. $\kappa_{s_{exp}}$ and z_{exp} indicates isentropic compressibility and acoustical impedance of binary mixtures. K represents the temperature dependent Jacobson constant.

Some inferences made from the Δk_s and Δz values are as follows

(i) All the binary mixtures show the negative values of Δk_s at all studied temperatures.

(ii) The highest negative values of Δk_s are observed for o-cresol containing binary mixtures. The negative values of Δk_s decrease with change of o-cresol to p-cresol in binary mixtures.

(iii) Similarly, the Δz values are negative for all the binary mixtures at all studied temperature.

(iv) The negative values of Δz shift toward more negative values with increase of temperature.

The negative value of $\Delta\kappa_s$ and the positive value of Δz indicate the presence of strong intermolecular interactions between the components of a binary mixture and the positive value of $\Delta\kappa_s$ and the negative value of Δz indicate the weak intermolecular interaction in binary mixture[22,23].

A perusal of Table S7-S9 (Supplementary Data), reveals that the o-cresol molecules show the highest intermolecular interaction with terpinolene molecules. Due to these interactions, the molecules try to orient closely with each other and result in the high speed of sound value, less isentropic compressibility, and high internal acoustical impedance[24,25].

The values of intermolecular free length (L_f) also support above given conclusion. The intermolecular free length (L_f) values of o-cresol binary mixture are small and with increase of temperature, the values are increasing. L_f values increase with change of o-cresol to p-cresol in binary mixtures indicating for the weakening of intermolecular interactions. On the basis of above given discussion of Δu, Δk_s, Δz and L_f, the order of interaction of cresols with terpinolene follows the order: .o-cresol > m-cresol > p-cresol.

Infinite Dilution Partial Molar Isentropic Compression$(\bar{K}^{o}_{s,m,i})$, *Excess Partial Molar Isentropic Compression*$(\bar{K}^{o,E}_{s,m,i})$ *and Apparent Molar Isentropic Compression*$(K_{s,m,\Phi,i})$

The calculated values of Infinite dilution partial molar isentropic compression$(\bar{K}^{o}_{s,m,i})$, excess partial molar isentropic compression$(\bar{K}^{o,E}_{s,m,i})$ and apparent molar isentropic compression$(K_{s,m,\Phi,i})$ for all binary mixtures over the entire composition range at all studied temperatures are listed in Table S10 of supplementary data. Graphical representation of $\bar{K}^{o}_{s,m,1}$, $\bar{K}^{o}_{s,m,2}$, $\bar{K}^{o,E}_{s,m,1}$, $\bar{K}^{o,E}_{s,m,2}$, $K_{s,m,\Phi,1}$, $K_{s,m,\Phi,2}$, $K'_{s,m,\Phi,1}$ and $K'_{s,m,\Phi,2}$ vs mole fraction (x_i)/ molality (m_i) is given as Figs. 5, 6 and S9-S14 (Supplementary Data), respectively.

These properties have been calculated using the following relations[21].

$$\bar{K}^{o}_{s,m,1} = K^{E}_{s,m} + K^{*}_{s,m,1} + x_2\left(\frac{\partial K^{E}_{s,m}}{\partial x_1}\right)_{T,P} \quad \ldots(28)$$

$$\bar{K}^{o}_{s,m,2} = K^{E}_{s,m} + K^{*}_{s,m,2} - x_1\left(\frac{\partial K^{E}_{s,m}}{\partial x_1}\right)_{T,P} \quad \ldots(29)$$

Taking differentiation of $\left(\frac{\partial K^{E}_{s,m}}{\partial x_1}\right)_{T,P}$ derivative, we get following relations.

$$\bar{K}^{o}_{s,m,1} = K^{*}_{s,m,1} + x_2^2\sum_{i=0}^{n} A_i(1-2x_1)^i - 2x_1x_2^2\sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \quad \ldots(30)$$

$$\bar{K}^{o}_{s,m,2} = K^{*}_{s,m,2} + x_1^2\sum_{i=0}^{n} A_i(1-2x_1)^i + 2x_1^2x_2\sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \quad \ldots(31)$$

$$\bar{K}^{o,E}_{s,m,1}\ ((TPa)^{-1}\cdot m^3\cdot\ mol^{-1}) = \bar{K}^{o}_{s,m,1} - K^{*}_{s,m,1} \quad \ldots(32)$$

$$\bar{K}^{o,E}_{s,m,2}\ ((TPa)^{-1}\cdot m^3\cdot\ mol^{-1}) = \bar{K}^{o}_{s,m,2} - K^{*}_{s,m,2} \quad \ldots(33)$$

where, $K^{E}_{s,m}$ represents excess molar isentropic copmpressibiity of mixture.$K^{*}_{s,m,1}$, $K^{*}_{s,m,2}$ and $\bar{K}^{o}_{s,m,1}$, $\bar{K}^{o}_{s,m,2}$ represents molar isentropic compression and partial molar isentropic compression of component 1 and 2, respectively.

Apparent molar isentropic compression$(K_{s,m,\phi,i})$ has been calculated using following two methods[13,21].

Method 1

$$K_{s,m,\phi,i} = \frac{\kappa_s M}{\rho} - \frac{1000\,(\kappa_{s_0}\rho - \kappa_s\rho_0)}{m\rho\,\rho_0} \quad \ldots(34)$$

Method 2

$$K'_{s,m,\phi,1} = \bar{K}^{0}_{s,m,1} + \left(\frac{K^{E}_{s,m}}{x_1}\right) \quad \ldots(35)$$

$$K'_{s,m,\phi,2} = \bar{K}^{0}_{s,m,2} + \left(\frac{K^{E}_{s,m}}{x_2}\right) \quad \ldots(36)$$

where, $K'_{s,m,\phi,i}$ represents apparent molar isentropic compression of ith component. κ_s, κ_{s_o}, ρ, $\rho_0$indicates isentropic compression of mixture, isentropic compression of solvent, density of mixture and solvent, respectively.

The calculated values of limiting apparent molar isentropic compression $(K^{o}_{s,m,\Phi,1})$ with empirical

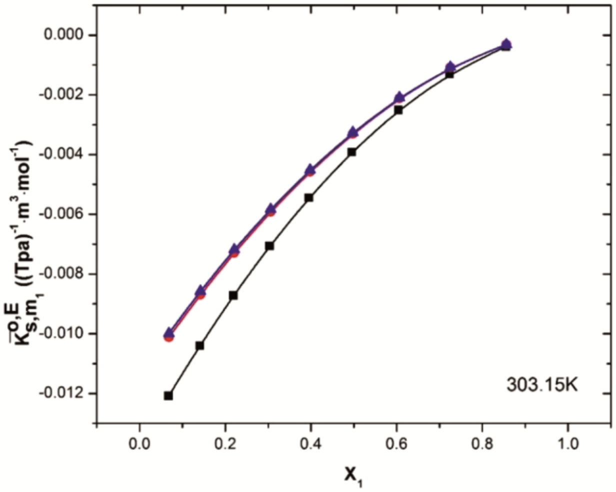

Fig. 5 — Infinite dilution excess partial molar isentropic compressibility $(\bar{K}^{o,E}_{s,m_1})$for the system Terpinolene (1) + o-, m-, and p-cresol (2) as a function of mole fraction at T = 303.15K: ■, Terpinolene (1) + o-cresol (2); ●, Terpinolene (1) + m-cresol (2); ▲, Terpinolene (1) + p-cresol (2).

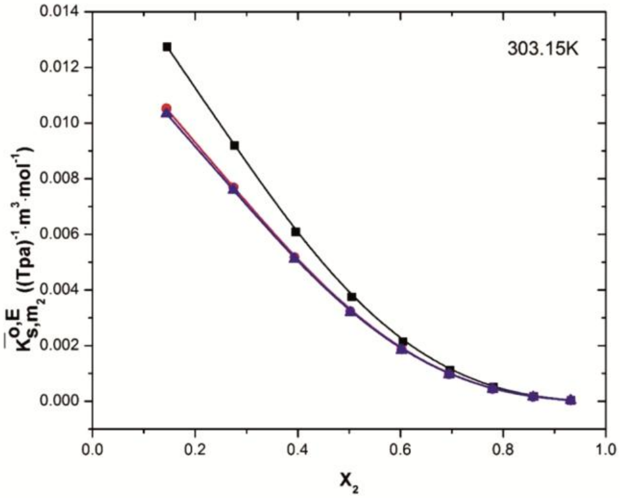

Fig. 6 — Infinite dilution excess partial molar isentropic compressibility $(\bar{K}^{o,E}_{s,m_2})$for the system Terpinolene (1) + o-, m-, and p-cresol (2) as a function of mole fraction at T = 303.15K: ■, Terpinolene (1) + o-cresol (2); ●, Terpinolene (1) + m-cresol (2); ▲, Terpinolene (1) + p-cresol (2).

parameters S_k and B_k of the Redlich-Rosenberg-Mayer equation and standard deviation (σ) are given in Table S11 (Supplementary Data). The limiting apparent molar isentropic compression ($K^{0}_{s.m.\phi,i}$) were calculated using the following Redlich-Rosenberg-Mayer equation[13,21].

$$K_{s,m,\phi,i}\ ((TPa)^{-1} \cdot m^3 \cdot mol^{-1}) = K^{0}_{s.m.\phi,i} + S_k m^{\frac{1}{2}} + B_k m \qquad \ldots(37)$$

where, $K^{0}_{s.m.\phi,i}$ represents limiting apparent molar isentropic compression of i^th^ component. S_k and B_k are the empirical parameters.

Some observations made from the values of $\overline{K}^{o}_{s,m,1}$, $\overline{K}^{o}_{s,m,2}$, $\overline{K}^{o,E}_{s,m,1}$, $\overline{K}^{o,E}_{s,m,2}$, $K_{s,m,\Phi,1}$, $K_{s,m,\Phi,2}$, $K'_{s,m,\Phi,1}$ and $K'_{s,m,\Phi,2}$ are as follows

(i) All the binary mixtures show the negative values of $\overline{K}^{o,E}_{s,m,1}$,

(ii) The highest negative value of $\overline{K}^{o,E}_{s,m,1}$ is observed for terpinolene + o-cresol binary mixtures.

(iii) The calculated values of apparent molar isentropic compressibility $K_{s,m,\Phi,i}$ and $K'_{s,m,\Phi,i}$ are very close in values.

As the discussion given in our earlier article[1], All the binary mixtures show the positive values of $K^{o}_{s,m,\Phi,1}$ at all studied temperatures that indicates there is solvent intrinsic compressibility of large sized substituted organic groups because of the presence of intermolecular free space that leads to the more compressibility to the solution[13,26].

All the calculated excess and deviation in properties such as V^{E}_{m}, Δu, $\Delta\kappa_s$, $K^{E}_{s,m}$ and Δz were fitted with fourth order form of the Redlich-Kister[27] polynomial equation for representing excess or deviation functions for binary and ternary mixtures. Their values are given in Table S2, S4, S7 and S8 (Supplementary Data).

$$(Y)^E = x_1(1 - x_1)\sum_{i=1}^{n} A_i (2x_1 - 1)^i \qquad \ldots(38)$$

where, Y^E = excess/ deviation properties. x_i, A_i represents mole fraction of i^th^ component and fitting coefficient. The standard deviation (σ) have been calculated using following relation.

$$\sigma(Y) = \left[\frac{\Sigma(Y^{E}_{exp} - Y^{E}_{cal})}{N-P}\right]^{\frac{1}{2}} \qquad \ldots(39)$$

where, Y^{E}_{exp} , Y^{E}_{cal} indicates experimental and calculated values of excess/deviation properties, respectively. N is the number of experimental points and p is the number of parameters of the Redlich-Kister equation.

Quantum computational calculations

The values of bond length (Å) between atoms and Mulliken charges of atoms of pure terpinolene, cresols and their binary mixture at 298.15 K are given in Table 6 and 7. The optimized structural orientation in the gas phase with some parameters/ in form of Mulliken charge, 3D-MESP, 2D-Electrostatic potential contour map (ESPCM) is shown as Fig. 7, 8 and Fig. S15 to S21 (Supplementary Data). Some observations made from tables and figures for pure components are as follows.

Terpinolene

(i) The carbon atoms C1, C3 and C10 of aliphatic methyl ($-CH_3$) group of terpinolene possesses negative charge and its values are -0.652313, -0.627268 and -0.565117 respectively. So the hydrogen atoms attached with C1-H11 (0.152455), H12 (0.132807) H13 (0.148665), with C3-H14 (0.152049), H15 (0.136493), H16 (0.149798) and with C10-24H (0.152099), 25H (0.146778), 26H (0.151807) possess positive charge.

(ii) Hydrogen atoms attached with C4 to C8 ring also possess some positive charge.

Cresols

(i) In cresol molecules, all the hydrogen atoms possess the positive charge and the oxygen (O) atom of $-OH$ group possesses negative charge. The H16 hydrogen atom attached with an oxygen atom in $-OH$ group possesses the highest positive charge among all hydrogen atoms of structure.

On the basis of above observations, there may be chances of delocalization interactions and H-bonding types of interactions between electropositive and electronegative atoms of terpinolene and cresols.

Considering the charges and electron density on atoms, there may be mainly two types of possible interactions between terpinolene and cresol molecule. In this study, only o-cresol's interaction with terpinolene case has been optimized because the cresols molecules have the same type of atoms so

Table 6 — Optimized geometric parameter of pure components (Terpinolene and o-Cresol) and their mixtures using DFT/B3LYP with 6-31+G (d,p) at 298.15 K

Terpinolene		o-Cresol		Terpinolene + o-Cresol (Theoretical- First possible interaction site)		Terpinolene + o-Cresol (Theoretical- Second possible interaction site)	
Bond	Bond length (A°)	Bond	Bond length (A°)	Bond	Bond length (A°)	Bond	Bond length (A°)
R(1,2)	1.5144	R(1,2)	1.3976	R(1,2)	1.5144	R(1,2)	1.5151
R(1,11)	1.0989	R(1,3)	1.3943	R(1,11)	1.0989	R(1,11)	1.1002
R(1,12)	1.0903	R(1,9)	1.0853	R(1,12)	1.0902	R(1,12)	1.0905
R(1,13)	1.0983	R(2,6)	1.4074	R(1,13)	1.0984	R(1,13)	1.0983
R(2,3)	1.5146	R(2,8)	1.3738	R(2,3)	1.5146	R(1,42)	3.0980
R(2,4)	1.3509	R(3,4)	1.3978	R(2,4)	1.3507	R(2,3)	1.5143
R(3,14)	1.0988	R(3,10)	1.0861	R(3,14)	1.0987	R(2,4)	1.3507
R(3,15)	1.0904	R(4,5)	1.3965	R(3,15)	1.0903	R(3,14)	1.0985
R(3,16)	1.0986	R(4,11)	1.0855	R(3,16)	1.0985	R(3,15)	1.0902
R(4,5)	1.5144	R(5,6)	1.4013	R(4,5)	1.5146	R(3,16)	1.0984
R(4,6)	1.5203	R(5,12)	1.0874	R(4,6)	1.5206	R(4,5)	1.5145
R(5,7)	1.5406	R(6,7)	1.5111	R(5,7)	1.5406	R(4,6)	1.5204
R(5,17)	1.0912	R(7,13)	1.0990	R(5,17)	1.0912	R(5,7)	1.5404
R(5,18)	1.1010	R(7,14)	1.0929	R(5,18)	1.1010	R(5,17)	1.0913
R(6,8)	1.5135	R(7,15)	1.0990	R(6,8)	1.5141	R(5,18)	1.1009
R(6,19)	1.1045	R(8,16)	0.9653	R(6,19)	1.1045	R(6,8)	1.5135
R(6,20)	1.0940			R(6,20)	1.0941	R(6,19)	1.1044
R(7,9)	1.5129			R(6,35)	3.7448	R(6,20)	1.0940
R(7,21)	1.1010			R(7,9)	1.5126	R(7,9)	1.5129
R(7,22)	1.0994			R(7,21)	1.1000	R(7,21)	1.1009
R(8,9)	1.3410			R(7,22)	1.0994	R(7,22)	1.0993
R(8,23)	1.0901			R(7,35)	3.5113	R(8,9)	1.3410
R(9,10)	1.5071			R(8,9)	1.3418	R(8,23)	1.0900
R(10,24)	1.0984			R(8,23)	1.0903	R(9,10)	1.5071
R(10,25)	1.0942			R(8,35)	3.1687	R(10,24)	1.0984
R(10,26)	1.0986			R(9,10)	1.5073	R(10,25)	1.0942
				R(9,35)	3.0340	R(10,26)	1.0986
				R(10,24)	1.0984	R(11,34)	3.4719
				R(10,25)	1.0944	R(13,34)	3.0707
				R(10,26)	1.0983	R(27,28)	1.3977
				R(10,35)	3.4313	R(27,29)	1.3942
				R(21,27)	3.7884	R(27,35)	1.0853
				R(21,34)	2.9563	R(28,32)	1.4072
				R(26,27)	3.7631	R(28,34)	1.3739
				R(26,34)	3.6732	R(29,30)	1.3978
				R(27,28)	1.3975	R(29,36)	1.0861
				R(27,29)	1.3945	R(30,31)	1.3963
				R(27,35)	1.0856	R(30,37)	1.0856
				R(28,32)	1.4071	R(31,32)	1.4015
				R(28,34)	1.3761	R(31,38)	1.0874
				R(29,30)	1.3978	R(32,33)	1.5110
				R(29,36)	1.0862	R(33,39)	1.0988
				R(30,31)	1.3963	R(33,40)	1.0930
				R(30,37)	1.0856	R(33,41)	1.0989
				R(31,32)	1.4015	R(34,42)	0.9657
				R(31,38)	1.0874		
				R(32,33)	1.5112		
				R(33,39)	1.0990		
				R(33,40)	1.0929		
				R(33,41)	1.0990		
				R(34,42)	0.9654		

Table 7 — Mulliken charge Values of optimized geometric structure of pure components (Terpinolene and o-Cresol) and their mixtures using DFT/B3LYP with 6-31+G (d,p) at 298.15 K

Terpinolene		o-Cresol		Terpinolene + o-Cresol (Theoretical- First possible interaction site)		Terpinolene + o-Cresol (Theoretical- Second possible interaction site)	
Atom	Charge(e)	Atom	Charge(e)	Atom	Charge(e)	Atom	Charge(e)
1 C	-0.652313	1 C	0.490781	1 C	-0.666833	1 C	-0.889347
2 C	0.542974	2 C	-0.723517	2 C	0.361488	2 C	0.736928
3 C	-0.627268	3 C	-0.346602	3 C	-0.623099	3 C	-0.615732
4 C	0.279503	4 C	0.037554	4 C	0.488855	4 C	0.239477
5 C	-0.28812	5 C	-0.855274	5 C	-0.386355	5 C	-0.252357
6 C	-0.743722	6 C	1.162954	6 C	-0.695853	6 C	-0.732484
7 C	-0.347282	7 C	-0.589603	7 C	-0.504419	7 C	-0.360476
8 C	-0.153484	8 O	-0.518345	8 C	-0.270760	8 C	-0.171968
9 C	0.274048	9 H	0.132625	9 C	0.592973	9 C	0.285151
10 C	-0.565117	10 H	0.124306	10 C	-0.526132	10 C	-0.559738
11 H	0.152455	11 H	0.120625	11 H	0.149420	11 H	0.142224
12 H	0.132807	12 H	0.117539	12 H	0.131602	12 H	0.133401
13 H	0.148665	13 H	0.164013	13 H	0.148156	13 H	0.159967
14 H	0.152049	14 H	0.164308	14 H	0.152215	14 H	0.157457
15 H	0.136493	15 H	0.164225	15 H	0.133767	15 H	0.136904
16 H	0.149798	16 H	0.354412	16 H	0.147312	16 H	0.150592
17 H	0.113423			17 H	0.112601	17 H	0.111281
18 H	0.153625			18 H	0.152364	18 H	0.154216
19 H	0.160313			19 H	0.158072	19 H	0.160949
20 H	0.131847			20 H	0.125125	20 H	0.133457
21 H	0.152834			21 H	0.175040	21 H	0.153338
22 H	0.13669			22 H	0.131645	22 H	0.137058
23 H	0.109099			23 H	0.100707	23 H	0.109930
24 H	0.152099			24 H	0.147956	24 H	0.152056
25 H	0.146778			25 H	0.140560	25 H	0.147172
26 H	0.151807			26 H	0.157848	26 H	0.152236
				27 C	0.979411	27 C	0.368844
				28 C	-1.078820	28 C	-0.750569
				29 C	-0.836988	29 C	-0.291254
				30 C	0.260591	30 C	0.034933
				31 C	-0.911022	31 C	-0.743835
				32 C	1.311396	32 C	1.215147
				33 C	-0.621264	33 C	-0.634121
				34 O	-0.503908	34 O	-0.514889
				35 H	0.144015	35 H	0.132025
				36 H	0.124630	36 H	0.124075
				37 H	0.119804	37 H	0.120499
				38 H	0.117337	38 H	0.117983
				39 H	0.164114	39 H	0.164443
				40 H	0.164566	40 H	0.163731
				41 H	0.163739	41 H	0.165018
				42 H	0.368142	42 H	0.356279

there may be equal chances for interactions. The difference in strength of interaction will be due to its different substitution position of -OH groups in ring.

1. **First possible interaction site-** Interaction between electronegative and lone pairs containing oxygen (O) atom of cresol molecule and H21 hydrogen atom attached with C7 carbon atom of terpinolene. (See Fig. 7 and S15, S16 (Supplementary Data)

2. **Second possible interaction site-** Interaction between electronegative and electron lone pairs containing oxygen (O) atom of cresol molecule and hydrogen atoms attached with C1 to C3 carbons ($-CH_3$ groups) of terpinolene (See Fig. 8 and S17, S18 in Supplementary Data).

A perusal of Table 6 and 7 shows the presence of hydrogen bonding or delocalization type interaction is

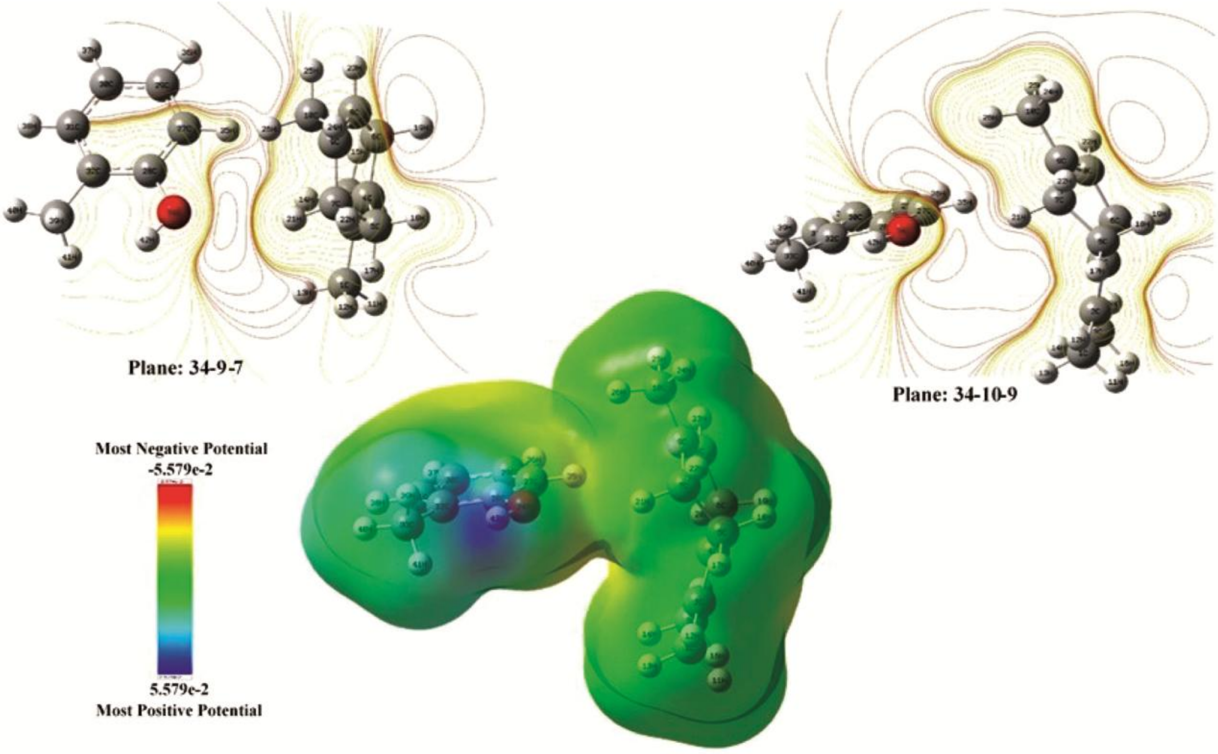

Fig. 7 — Optimized geometric structures of Terpinolene + o-Cresol binary mixture (first possible interaction site) in form of 3D MESP Surface and 2D electrostatic potential contour map based on B3LYP/6-31+G(d,p) at 298.15 K.

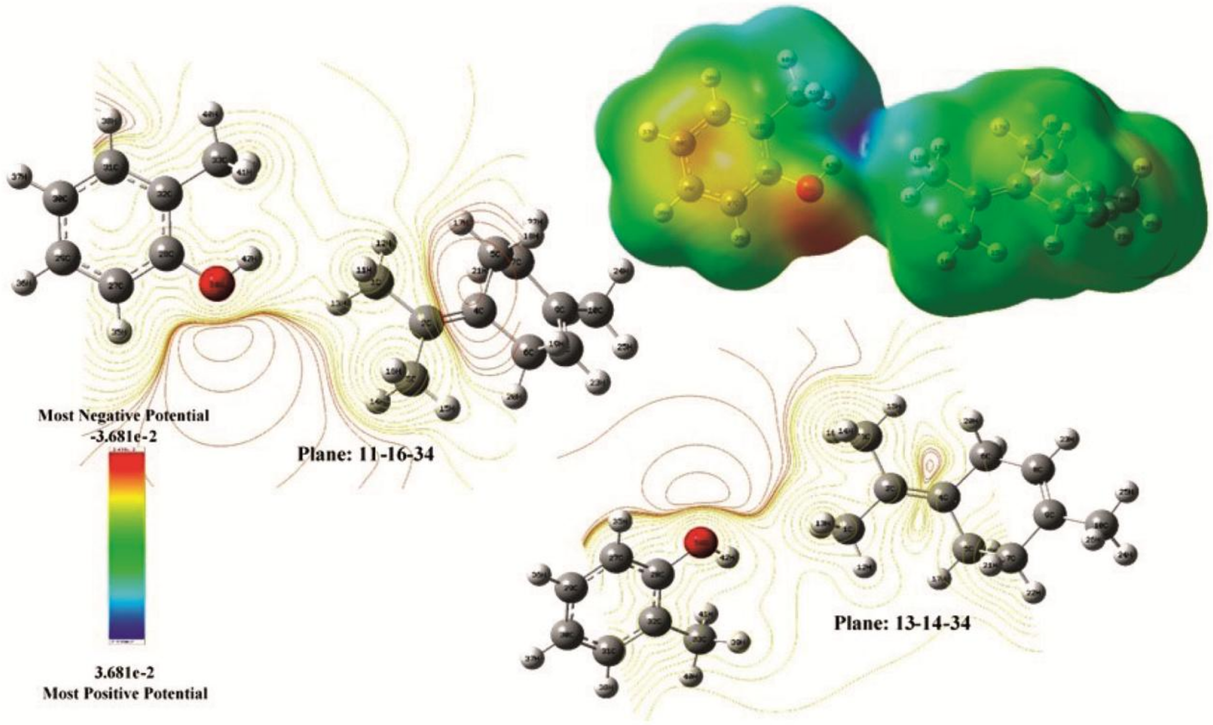

Fig. 8 — Optimized geometric structures of Terpinolene + o-Cresol binary mixture (second possible interaction site) in form of 3D MESP Surface and 2D electrostatic potential contour map based on B3LYP/6-31+G(d,p) at 298.15 K.

considered as possible interaction site. Considering the first possible interaction site, where O34 (oxygen) and H21 atoms involve in H-bonding. C28-O34 and O34-H42 bonds act as proton acceptors (electron density donor) and C7-H21 bond act as a proton donor (electron density acceptor). So due to extraction of electron density from C28-O34 and O34-H42 bonds to H21-C7 bond, the C28-O34 and O34-H42 bonds increase their bond length and H21-C7 bond decrease its bond length. The initial bond length of H21-C7 of terpinolene molecule and C28-O34 and O34-42H bonds of o-cresol molecule was 1.1010, 1.3738 and 0.9653 Å, respectively. In first possible interaction site of terpinolene + o-cresol, the value has changed to 1.1000, 1.3761 and 0.9654 Å, respectively.

Similarly, values of Mulliken charges also support the above given discussion, formation of H-bonding and presence of intermolecular interactions between components of binary mixtures. The initial charge value of C7 and H21 atoms of terpinolene molecule and C28, O34, H42 atoms of o-cresol molecule in pure gaseous phase are -0.347282, 0.152834, -0.723517, -0.518345 and 0.354412 (e), respectively. In first possible interaction site, the values of Mulliken charge of these atoms change to -0.504419, 0.175040, -1.078820, -0.503908 and 0.368142 (e), respectively.

Similarly, the results of bond length and Mulliken charges in the case of second possible interaction site of terpinolene + o-cresol binary mixture also support the presence of intermolecular interactions between terpinolene + cresols.

NBO Analysis

The second order perturbation energy calculations from NBO analysis supports the presence of intermolecular interaction between different atoms of components of binary mixtures due to the delocalization type interaction between lone pairs of oxygen (O) atom and antibonding (σ^*) orbital of nearer $C-H$ bond of terpinolene. The detailed values of energies associated with different interactions are shown in Table8 and some of are discussed as follows.

1. Terpinolene + o-cresol

(I) First possible interaction site

(a) Interaction from terpinolene to o-cresol

(i) Interaction between σ_{C8-C9} → $\sigma^*_{C27-H35}$ with energy value of 0.60 $kcal \cdot mol^{-1}$.

(b) Interaction from o-cresol to terpinolene

(i) Interaction between O34 lone pair (1) → σ^*_{C7-H21} with energy value of 0.37 $kcal \cdot mol^{-1}$.

(II) Second possible interaction site

(a) Interaction from terpinolene to o-cresol

(i) Interaction between σ_{C1-H11} → $\sigma^*_{O34-H42}$ with energy value of 0.06 $kcal \cdot mol^{-1}$.

(b) Interaction from o-cresol to terpinolene

(i) Interaction between $\sigma_{O34-H42}$ → $RY^*(1)_{H13}$ with energy value of 0.06 $kcal \cdot mol^{-1}$.

(ii) Interaction between O34 lone pair (1) → $RY^*(4)_{C2}$ with energy value of 0.10 $kcal \cdot mol-1$.

The second order perturbation energy calculations of NBO analysis (Table 8) shows the presence of delocalization type intermolecular interaction between the lone pair of the oxygen atom and antibonding (σ^*) of nearer C-H bond.

Experimental FTIR and theoretical vibrational analysis

For getting information about the formation of hydrogen bonding or presence of some other intermolecular associations between the atoms of components of binary mixtures, the FTIR spectra of

Table 8 — Second order perturbation energies (E(2)/$kcal \cdot mol^{-1}$) of Hydrogen bonds and interactions obtained by NBO calculation using B3LYP/6-31+G(d,p).

Association	Donor NBO (i)	Acceptor NBO (j)	E(2)/ $kcal \cdot mol-1$
Terpinolene (1) + o-Cresol (2)			
First Possible Interaction Site			
From Unit 1 to Unit 2 (Terpinolene to o-Cresol)			
1	BD (2) C8 - C9	BD*(1) C27 - H35	0.60
From Unit 2 to Unit 1 (o-Cresol to Terpinolene)			
1	LP (1) O34	RY*(4) C9	0.07
2	LP (1) O34	BD*(1) C7 - H21	0.37
Second Possible Interaction Site			
From Unit 1 to Unit 2 (Terpinolene to o-Cresol)			
1	BD (1) C1 - H11	BD*(1) O34 - H42	0.06
From Unit 2 to Unit 1 (o-Cresol to Terpinolene)			
1	BD (1) O34 - H42	RY*(1) H13	0.06
2	LP (1) O34	RY*(4) C2	0.10

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

pure components and their binary mixtures at three different composition ratio such as 4:1, 1:1 and 1:4 were recorded at 298.15 K. Considering the results of computational analysis, the test is mainly focused on functional groups frequencies which may contribute to interactions present in these binaries. These frequencies are intermolecular H-bonding (v_{O---H}), aliphatic $C-H$ symmetrical stretching (v_{C-H}), aromatic $C-H$ symmetrical stretching (v_{C-H})of terpinolene and aliphatic $C-H$ symmetrical stretching (v_{C-H}), aromatic $C-H$ symmetrical stretching (v_{C-H}), free phenolic $-OH$ stretching (v_{O-H}) and $C-O$ stretching (v_{C-O}) of cresol.

The experimentally obtained frequencies values of pure components and their binary mixtures as well as the values of theoretically calculated frequencies using B3LYP/6-31+G(d,p) method with their shift values with comparison respect to terpinolene and cresols are listed in Table 9. The spectra of pure components and binary mixtures at different composition ratios are as showed in Fig. 9 to 11 and Fig. S22 to S33 (Supplementary Data).

Table 9 — Experimental FTIR and theoretical IR frequencies with wavenumbers (cm^{-1}) and shifting of bands of Terpinolene (1) + o-, m- and p-Cresol (2) binary mixtures at 298.15 K

Component/ Mixture		Intermolecular H-bonding $v_{o\ldots H}$			Free Phenolic –OH symmetrical stretching v_{O-H}			Aliphatic C-H symmetrical stretching v_{C-H}			Aromatic C-H symmetrical stretching v_{C-H}			Cresol C-O stretching v_{C-O}		
		Exp.	Theoretical		Exp.	Theoretical		Exp.	Theoretical		Exp.	Theoretical		Exp.	Theoretical	
			Scaled	Un-scaled		Scaled	Un-scaled		Scaled	Un-scaled		Scaled	Un-scaled		Scaled	Un-scaled
Terpinolene		-	-	-	-	-	-	2909.01	2906.65 (T-10) 2912.32 (T-1,3)	3015.20 (T-10) 3021.08 (T-1,3)	3017.40	3004.45 (T-5) 2968.91 (T-6) 2925.21 (T-7) 3029.62 (T-8)	3116.65 (T-5) 3079.78 (T-6) 3034.45 (T-7) 3142.76 (T-8)	-	-	-
o-Cresol		3417.12	-	-	3778.53	3702	3840	2920.35	2902.41	3010.80	3033	3088	3203	1242	1240.04	1286.35
m-Cresol		3330.66	-	-	3755.85	3690	3828	2921	2925	3035	3039.4	3084	3200	1266.36	1257	1364
p-Cresol		3331.37	-	-	3779.24	3692	3829	2921.77	2922	3031	3023.81	3068/ 3059	3183/ 3174	1236.60	1237	1283
Terpinolene + o-Cresol Experimental	4:1	3382.39	-	-	3646.01	-	-	2911.14	-	-	3017.44	-	-	1238.72	-	-
	1:1	3396.56	-	-	Not Seen	-	-	2916.10	-	-	3029.48	-	-	1242.27	-	-
	1:4	3417.12	-	-	3747.35	-	-	2918.93	-	-	3032.32	-	-	1241.56	-	-
Terpinolene + m-Cresol Experimental	4:1	3377.43	-	-	3751.6	-	-	2912.56	-	-	3016.73	-	-	1257.15	-	-
	1:1	3362.55	-	-	Not Seen	-	-	2913.26	-	-	3039.40	-	-	1267.78	-	-
	1:4	3346.25	-	-	3756.56	-	-	2921.06	-	-	3039.40	-	-	1267.07	-	-
Terpinolene + p-Cresol Experimental	4:1	3382.39	-	-	3674.36	-	-	2911.14	-	-	3016.02	-	-	1225.97	-	-
	1:1	3356.88	-	-	Not Seen	-	-	2914.68	-	-	3019.56	-	-	1227.38	-	-
	1:4	3333.49 Broad	-	-	3778.53	-	-	2921.06	-	-	3023.11	-	-	1235.89	-	-
Terpinolene + o-Cresol (Theoretical- First possible interaction site)		-	-	-	-	3699.92	3838.09	-	2907.98 (T-10) 2912.22 (T-1,3) 2901.92 (C-33)	3016.58 (T-10) 3020.98 (T-1,3) 3010.29 (C-33)	-	3026.37 (T-8) 2931.44 (T-7) 3094.01 (C-all carbons)	3139.39 (T-8) 3040.91 (T-7) 3209.55 (C-all carbons)	-	1238.37	1284.62
Terpinolene + o-Cresol (Theoretical- Second possible interaction site)		-	-	-	-	3694.89	3832.87	-	2906.91 (T-10) 2898.14 (T-1) 2912.29 (T-3,1) 2901.92 (C-33)	3015.47 (T-10) 3006.37 (T-1) 3021.05 (T-3,1) 3012.66 (C-33)	-	3030.21 (T-8) 2926.18 (T-7) 3096.42 (C-all carbons)	3143.37 (T-8) 3035.46 (T-7) 3212.06 (C-all carbons)	-	1240.57	1286.90

(*Contd.*)

Table 9 — Experimental FTIR and theoretical IR frequencies with wavenumbers (cm^{-1}) and shifting of bands of Terpinolene (1) + o-, m- and p-Cresol (2) binary mixtures at 298.15 K. (*Contd.*)

Terpinolene + o-Cresol (Theoretical-Solvation)		-	-	-	-	-	-	-	2911.58 (T-1,3) 2906.27 (T-10)	3020.31 (T-1,3) 3014.80 (T-10)	-	3005.58 (T-5) 2971.59 (T-6) 2926.14 (T-7) 3027.88 (T-8)	3117.82 (T-5) 3082.56 (T-6) 3035.42 (T-7) 3140.95 (T-8)	-	-	-
Terpinolene + m-Cresol (Theoretical-Solvation)		-	-	-	-	-	-	-	2911.53 (T-1,3) 2906.26 (T-10)	3020.26 (T-1,3) 3014.79 (T-10)	-	3005.83 (T-5) 2971.96 (T-6) 2926.55 (T-7) 3027.66 (T-8)	3118.08 (T-5) 3082.95 (T-6) 3035.84 (T-7) 3140.73 (T-8)	-	-	-
Shift in wavenumber with respect to pure Terpinolene values																
Terpinolene + o-Cresol Experimental	4:1	-	-	-	-	-	-	2.13	-	-	0.04	-	-	-	-	-
	1:1	-	-	-	-	-	-	7.09	-	-	12.08	-	-	-	-	-
	1:4	-	-	-	-	-	-	9.92	-	-	14.92	-	-	-	-	-
Terpinolene + m-Cresol Experimental	4:1	-	-	-	-	-	-	3.55	-	-	-0.67	-	-	-	-	-
	1:1	-	-	-	-	-	-	4.25	-	-	22.00	-	-	-	-	-
	1:4	-	-	-	-	-	-	12.05	-	-	22.00	-	-	-	-	-
Terpinolene + p-Cresol Experimental	4:1	-	-	-	-	-	-	2.13	-	-	-1.38	-	-	-	-	-
	1:1	-	-	-	-	-	-	5.67	-	-	2.16	-	-	-	-	-
	1:4	-	-	-	-	-	-	12.05	-	-	5.71	-	-	-	-	-
Terpinolene + o-Cresol (Theoretical-First possible interaction site)		-	-	-	-	-	-	-	1.33 (T-10) -0.1 (T-1,3)	1.38 (T-10) -0.1 (T-1,3)	-	-3.25 (T-8) 6.23 (T-7)	-3.37 (T-8) 6.46 (T-7)	-	-	-
Terpinolene + o-Cresol (Theoretical-Second possible interaction site)		-	-	-	-	-	-	-	0.26 (T-10) -0.03 (T-1,3)	0.27 (T-10) -0.03 (T-1,3)	-	0.59 (T-8) 0.97 (T-7)	0.61 (T-8) 1.01 (T-7)	-	-	-
Terpinolene + o-Cresol (Theoretical-Solvation)		-	-	-	-	-	-	-	-0.74 (T-1,3) -0.38 (T-10)	-0.77 (T-1,3) -0.40 (T-10)	-	1.13 (T-5) 2.68 (T-6) 0.93 (T-7) -1.74 (T-8)	1.17 (T-5) 2.78 (T-6) 0.97 (T-7) -1.81 (T-8)	-	-	-
Terpinolene + m-Cresol (Theoretical-Solvation)		-	-	-	-	-	-	-	-0.79 (T-1,3) -0.40 (T-10)	-0.82 (T-1,3) -0.41 (T-10)	-	1.38 (T-5) 3.06 (T-6) 1.34 (T-7) -1.96 (T-8)	1.43 (T-5) 3.17 (T-6) 1.39 (T-7) -2.03 (T-8)	-	-	-
Shift in wavenumbers with respect to Cresols values																
Terpinolene + o-Cresol Experimental	4:1	-34.73	-	-	-132.52	-	-	-9.21	-	-	-15.56	-	-	-3.28	-	-
	1:1	-20.56	-	-	-	-	-	-4.25	-	-	-3.52	-	-	0.27	-	-
	1:4	0	-	-	-31.18	-	-	-1.42	-	-	-0.68	-	-	-0.44	-	-
Terpinolene + m-Cresol Experimental	4:1	46.77	-	-	-4.25	-	-	-8.44	-	-	-22.67	-	-	-9.21	-	-
	1:1	31.89	-	-	-	-	-	-7.74	-	-	0	-	-	1.42	-	-
	1:4	15.59	-	-	0.71	-	-	0.06	-	-	0	-	-	0.71	-	-

(*Contd.*)

Table 9 — Experimental FTIR and theoretical IR frequencies with wavenumbers (cm^{-1}) and shifting of bands of Terpinolene (1) + o-, m- and p-Cresol (2) binary mixtures at 298.15 K (*Contd.*)

Terpinolene + p-Cresol Experimental	4:1	51.02	-	-	-104.88	-	-	-10.63	-	-	-7.79	-	-	-10.63	-	-
	1:1	25.51	-	-	-	-	-	-7.09	-	-	-4.25	-	-	-9.22	-	-
	1:4	2.12	-	-	-0.71	-	-	-0.71	-	-	-0.7	-	-	-0.71	-	-
Terpinolene + o-Cresol (Theoretical- First possible interaction site)		-	-	-	-	-1.84	-1.91	-	-0.49 (C-33)	-0.51 (C-33)	-	6.31 (C- all carbons)	6.55 (C- all carbons)	-	-1.67	-1.73
Terpinolene + o-Cresol (Theoretical- Second possible interaction site)		-	-	-	-	-6.87	-7.13	-	1.79 (C-33)	1.86 (C-33)	-	8.73 (C-all carbons)	9.06 (C-all carbons)	-	0.53	0.55
Terpinolene + o-Cresol (Theoretical- Solvation)		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Terpinolene + m-Cresol (Theoretical- Solvation)		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

The Standard Uncertainty U is U(T) = 0.1K. All spectra are taken at atmospheric pressure and composition of binary mixture is 4:1, 1:1, and 1:4. Theoretical spectra are calculated using B3LYP/6-31+G(d,p)

(T-5-8) = this frequency is contributed from Terpinolene molecule's hydrogen atom/s attached with C5-C8 atom

(T-1,3) = this frequency is contributed from Terpinolene molecule's hydrogen atom/s attached with C1 and C3 atoms

(C-33) = this frequency is contributed from Cresol molecule's hydrogen atom/s attached with C33 atom

(C-all carbons) = this frequency is contributed from Cresol molecule's hydrogen atoms attached with Carbon atoms of aromatic ring

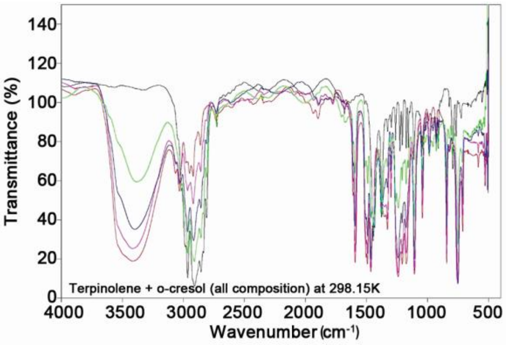

Fig. 9 — Experimental FTIR transmittances spectra at 298.15K for Terpinolene (1) + o-Cresol (2);▬▬,pure o-Cresol; ▬▬, 4:1 composition ratio; ▬▬, 1:1 composition ratio; ▬▬,1:4 composition ratio and ▬▬,pure Terpinolene.

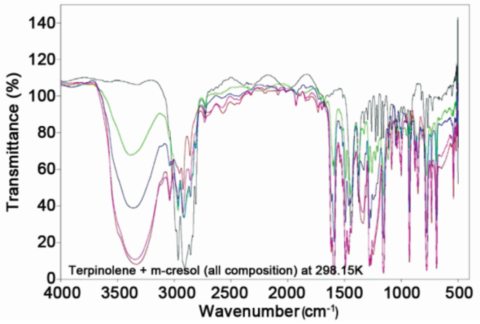

Fig. 10 — Experimental FT-IR transmittances spectra at 298.15K for Terpinolene (1) + m-Cresol (2);▬▬,pure m-Cresol; ▬▬, 4:1 composition ratio; ▬▬, 1:1 composition ratio; ▬▬,1:4 composition ratio and ▬▬,pure Terpinolene.

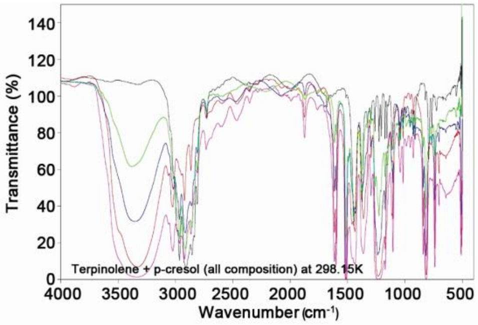

Fig. 11 — Experimental FTIR transmittances spectra at 298.15K for Terpinolene (1) + p-Cresol (2);▬▬,pure p-Cresol; ▬▬, 4:1 composition ratio; ▬▬, 1:1 composition ratio; ▬▬,1:4 composition ratio and ▬▬,pure Terpinolene.

The standard characteristics IR frequencies for selected functional groups are 3200–3600 cm^{-1} for hydrogen bonding (v_{O---H}), 3500–3700 cm^{-1} free phenolic $-OH$ stretching (v_{O-H}), 3000–2850 cm^{-1} for aliphatic $C-H$ symmetrical stretching (v_{C-H}), 3000–3100 cm^{-1} for aromatic $C-H$ symmetrical stretching (v_{C-H}) and 1000–1260 cm^{-1} for cresol's $C-O$ stretching (v_{C-O})[28,29].

As per the results of computational analysis, it is found that the hydrogen atoms of terpinolene molecules are involved in hydrogen bonding or delocalization type interactions with lone pairs of oxygen (O) atom of cresol. The $C-H$ bond of terpinolene (aromatic/aliphatic) act as an electron density acceptor (proton donor) and $O-H$, $C-O$ bonds of cresol act as an electron density donor (proton acceptor). So the increase in electron density in $C-H$ bonds of terpinolene, they require some higher energy for stretching in IR and results in a blue shift. Reverse phenomenon is observe for $C-O$ and $O-H$ bonds' stretching of cresol and result in a red shift.

So, the shift values of $C-H$ stretching frequencies with respect to terpinolene frequencies of pure state are positive. The shift values of H-bonding (v_{O---H}) stretching, free phenolic $-OH$ stretching (v_{O-H}) and cresol's $C-O$ stretching (v_{C-O}) with respect to pure cresol's values are negative. These shift values indicate the presence of delocalization type strong intermolecular interaction between atoms of binary mixture's components.

In o-cresol containing binary mixtures, the strength of H-bonding is stronger than it is in pure o-cresol. At 4:1 composition ratio of terpinolene and o-cresol, the strength of H-bonding is the strongest in comparison of the other composition ratios. The strength of newly formed H-bonding is weak with respect to it is in pure cresol state for m-cresol and p-cresol binary mixtures.

Conclusions

The magnitude of negative values of V_m^E, $\bar{V}_{m,1}^{o,E}$, Δk_s, $\bar{K}_{s,m,1}^{o}$, Δz and positive values of $V_{m,\Phi,1}^{o}$, E_{Φ}^{o}, Δu indicates the presence of strong intermolecular interactions between components of binary mixtures.The values of these quantities decrease with increase of temperature indicating that the strength of interactions decrease at higher temperature. The values of empirical parameters such as S_v, B_v and S_k, B_k of the Redlich-Rosenberg-Mayer equation also support the presence of electrostatic types intermolecular interactions. FTIR spectral analysis indicates the formation of H-bonding between lone pairs containing electronegative O (oxygen) atom of $-OH$ group of cresol and positively charged hydrogen atoms of terpinolene molecules. The computational analysis also supports the H-bonding formation and the presence of delocalization type interaction between different atomic sites. The second order perturbation energies obtained from NBO analysis shows that the strongest interactions are observed in first possible interaction site. The interaction strength order for cresols with terpinolene is o-cresol > m-cresol > p-cresol.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA 56A (06) 797-815_SupplData.pdf.

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