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Volumetric, viscometric, optical, acoustical and spectral investigations of intermolecular interactions in ternary mixtures of terpinolene and α-terpineol with cresols

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Densities (ρ), viscosities (η), refractive indexes (n_D) and speed of sound (u) have been measured experimentally for ternary mixtures of terpinolene, α-terpineol 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), deviation in viscosities $(\Delta\eta)$, excess Gibbs' free energy of activation of viscous flow (ΔG^{*E}) deviation in refractive index (Δn_D), 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), and intermolecular free length (L_f) have been calculated. 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 have also been calculated. FT-IR spectral analysis of ternary mixtures at 1:1:1, 2:1:1, 1:2:1 and 1:1:2 composition ratios have been carried out at 298.15 K. The results have been discussed in term of presence of intermolecular interactions, their types, strength and behavior change with change in temperatures and change in ratio of components in ternary mixtures.

Keywords: Density, Viscosity, Refractive index, Speed of sound, FT-IR, Intermolecular interactions, Deviation properties

In recent years, the exploration of intermolecular interactions in complex chemical systems has gained considerable attention, owing to its significance in understanding the thermodynamic and spectroscopic behavior of multi-component mixtures. Ternary mixtures, in particular, offer a rich domain for investigation due to the intricate interplay of diverse molecular species. The present study delves into the comprehensive analysis of ternary mixtures comprising terpinolene, α-terpineol, and cresols, with a focus on elucidating the intricacies of their intermolecular interactions.

In continuation of our prior work on binary mixtures of terpinolene with cresols, as published in this journal[1,2], the current research represents a logical extension that further explores the intricate landscape of intermolecular interactions within ternary mixtures. Our previous investigation provided valuable insights into the binary systems, and the present study aims to broaden our understanding by delving into the complexities introduced in ternary combinations.

Terpinolene and α-terpineol, both belonging to the family of terpenoids, exhibit distinctive structural features and possess diverse functional groups[3-5]. The inclusion of these compounds in ternary mixtures introduces a layer of complexity that warrants a meticulous investigation. The cresol isomers, namely *o*-cresol, *m*-cresol, and *p*-cresol, are aromatic compounds with variations in substitution patterns, offering a spectrum of potential interactions within the ternary system.

Understanding the physicochemical properties of such ternary mixtures is essential for various industrial applications, including formulation in perfumery, pharmaceuticals, and chemical processes[6,7]. The behavior of these mixtures under different temperature conditions and at atmospheric pressure is a critical aspect of their practical utility.

The present work focuses on a multi-faceted approach by employing volumetric, viscometric, optical, acoustical, and spectral analyses to unravel the intricacies of intermolecular interactions within the ternary mixtures. By investigating primary properties such as density, viscosity, refractive index, and speed of sound, as well as deriving secondary properties like molar volume, excess molar volume, and acoustical impedance, *etc*., we aim to provide a comprehensive understanding of the thermodynamic and spectroscopic behavior of these mixtures.

The exploration of excess/deviation properties, analyzed through the Redlich-Kister polynomial equation, enables the quantification of the deviations from ideality and sheds light on the specific nature and strength of intermolecular interactions. Furthermore, the FT-IR spectral analysis at various composition ratios offers insights into the molecular-level changes, facilitating a deeper understanding of the composition-dependent behavior.

In summary, this research contributes to the existing body of knowledge in the field of chemical interactions by offering a systematic and detailed investigation into ternary mixtures, providing valuable insights for both academic and industrial applications. The discussion of results will not only enhance our understanding of these specific ternary systems but also contribute to the broader understanding of intermolecular interactions in complex chemical mixtures.

Experimental Section

Materials

The chemicals employed in this investigation were of analytical reagent (AR) grade purity and underwent purification through established methods[8,9]. Additional specifics, including information on suppliers, purification techniques, CAS numbers, and the method used for the final purity analysis, can be found in Table S1. A comprehensive comparative analysis of the experimental results and literature values for densities, viscosities, refractive indexes, and the speed of sound for the individual components is presented in Table 1. The observed values closely align with those reported in the literature, underscoring the reliability and consistency of our experimental outcomes.

Apparatus and Procedure

Sample Preparation

The ternary mixtures were prepared by blending precise masses of individual components, facilitated by an electronic balance (Reptech RA-2012) with an accuracy of ± 0.0001g. To mitigate the risk of contamination and solvent loss attributable to evaporation, each mixture was concocted within glass

Table 1— Experimental and literature values of Densities $(\boldsymbol{\rho})$, Viscosities $(\boldsymbol{\eta})$, Refractive indexes $(\boldsymbol{n_D})$ and Speed of sound $(\boldsymbol{u})$ of pure components at 303.15, 308.15 and 313.15K.

Pure Component	T/K	ρ /(gm·cm^3)		η /(mPa·s)		n_D		u/(m·s^{-1})	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Terpinolene	303.15	0.853890	–	1.007	–	1.4860	–	1350.48	–
	308.15	0.849991	–	0.945	–	1.4843	–	1330.99	–
	313.15	0.846075	–	0.884	–	1.4821	–	1311.33	–
α-Terpineol	303.15	0.928076	–	24.387	–	1.4804	–	1407.52	–
	308.15	0.924122	–	16.828	–	1.4783	–	1389.73	–
	313.15	0.920118	–	12.159	–	1.4762	–	1372.18	–
o-Cresol	303.15	1.037029	1.0369[14] 1.0487[15]	5.935	–	1.5412	1.5410[14]	1487.70	1487[14]
	308.15	1.032655	1.0316[14] 1.03273[16]	4.849	–	1.5390	1.5386[16] 1.5370[14]	1470.56	1478[21] 1470[14]
	313.15	1.028261	1.0260[17] 1.0391[16]	4.032	4.243[17]	1.5364	–	1453.38	1462[15]
m-Cresol	303.15	1.026135	1.0261[18]	9.922	9.806[18]	1.5357	1.5350[14]	1465.61	1465[14]
	308.15	1.022187	1.02164[19]	7.824	7.701[19]	1.5342	1.5320[14]	1449.94	1450[14]
	313.15	1.018215	1.0160[17]	6.349	6.252[17] 6.120[19]	1.5319	–	1434.28	–
p-Cresol	303.15	1.025991	1.0263[14]	10.927	–	1.5353	1.5340[14]	1472.23	1471[14]
	308.15	1.022115	1.02198[20] 1.0224[14]	8.646	8.444[20]	1.5338	1.5310[14]	1456.73	1455[14]
	313.15	1.018204	1.0168[17] 1.01805[20]	6.949	6.661[17] 6.745[20]	1.5305	–	1441.02	–

Standard uncertainties u, $u(T)$ = ±0.01 K, $u(\rho)$ = ±0.000001 gm·cm3, $u(\eta)$ = ±0.001 mPa·s, $u(n_D)$ = ±0.0001 and $u(u)$ = ±0.000001 m·s^{-1}. All physical quantities are measured at atmospheric pressure.

stopper flasks. These flasks were then stored in a dark environment to preempt any potential photolytic impact on the mixtures. The estimated uncertainty in the mole fraction was ± 0.0001.

Density (ρ) and Speed of Sound (u) measurement

Density and speed of sound values for all the individual components and their ternary mixtures were measured utilizing an automated density and speed of sound measuring meter, specifically the DSA 5000 M model by Anton Paar, India. The instrument is having a remarkable measuring accuracy of ±0.000005 $g{\cdot}cm^{-1}$ for density and ±0.1 $m{\cdot}s^{-1}$ for the speed of sound. Throughout the measurement process, temperature control was upheld through an inbuilt system with an impressive accuracy of ±0.001°C (0.002°F). Calibration of the instrument was executed with highly pure deionized water provided by the manufacturer, ensuring the reliability and precision of the acquired data.

Viscosity (η) measurement

Viscosity values for the individual components and their ternary mixtures were measured utilizing an Ubbelohde suspended level viscometer, procured from Agarwal Scientific Glass Company in Mumbai, India. For precise calibration, the A and B constants of the viscometer were determined by measuring the flow times of double-distilled water at temperatures of 303.15, 308.15, and 313.15 K. Temperature control during viscosity measurements was achieved through a thermostatic water bath (Model No.: 14L-SS, Equiptron Water Bath Company, India), with its accuracy at ± 0.01°C. The estimated precision in the viscosity value was maintained at ± 0.001 mPa·s.

Refractive index (n_D) measurement

The determination of the refractive index values for the individual components and their ternary mixtures were accomplished employing a thermostated Abbe's refractometer (SER No. 995033). The calibration of the refractometer involved the use of precisely determined refractive indices of 1-bromonaphthalene, methanol, and double-distilled water. To ensure accuracy during refractive index measurements, the temperature control was maintained through the circulation of water, facilitated by a pump integrated with a thermostatic water bath (Model No. 14L-SS, Equiptron Water Bath Company, India), having an accuracy of ± 0.01°C. The estimated precision of refractive index measurements was upheld at ± 0.0001.

FT-IR measurement

Fourier-transform infrared (FTIR) spectra for the individual components and their ternary mixtures were recorded utilizing an alpha – FTIR spectrometer from Bruker, Germany. The measurements were conducted with a high resolution of 2 cm^{-1} and a scan rate of 4 scans at 298.15 K. Spectra were systematically recorded at composition ratios of 1:1:1, 2:1:1, 1:2:1 and 1:1:2 (v/v %) to comprehensively assess the variations across different concentrations. To enhance the accuracy of the FTIR spectra, corrections were applied for water vapor and CO_2 contributions, ensuring the fidelity of the obtained spectral data.

Results and Discussion

Density (ρ) and Excess Partial Molar Volume (V_m^E)

The investigation of density (ρ) and excess partial molar volume (V_m^E) for ternary mixtures comprising Terpinolene (1), α-Terpineol (2), and *o*-, *m*-, and *p*-Cresol (3) at temperatures 303.15 K, 308.15 K, and 313.15 K reveals valuable insights into the intermolecular interactions within the system. The experimental density values (ρ) and calculated excess partial molar volumes (V_m^E) across the entire composition range are presented in Table S2. Additionally, the graphical representation of (V_m^E) *versus* mole fraction (x_1, x_2, x_3) at 303.15 K is depicted in Fig. 1. The associated fitting coefficients $(A_{ijk}, B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk})$ of the Redlich-Kister polynomial equation for (V_m^E), along with standard deviation (σ), are detailed in Table S3.

The following mathematical relations have been employed to calculate the molar volumes (V_m) and excess molar volume (V_m^E) for pure components and mixtures, respectively

$$V_i(cm^3.mol^{-1}) = M_i/\rho_i \quad \text{... (1)}$$

$$V_m(cm^3.mol^{-1}) = M_1x_1 + M_2x_2/\rho_m \quad \text{... (2)}$$

$$V_m^E(cm^3.mol^{-1}) = \left(\frac{x_1M_1+x_2M_2}{\rho_m}\right) - \left(\frac{x_1M_1}{\rho_1}\right) - \left(\frac{x_2M_2}{\rho_2}\right) - \left(\frac{x_3M_3}{\rho_3}\right) \quad \text{... (3)}$$

$$V_m^E(cm^3.mol^{-1}) = V_m - V_1x_1 - V_2x_2 - V_3x_3 \quad \text{... (4)}$$

Here, V_m, V_1, V_2, and V_3 represent the molar volumes of the mixture, component 1, component 2, and component 3, respectively. x_1, x_2, x_3 & M_1, M_2, and M_3 represent the mole fractions and molar masses of components 1, 2, and 3, respectively. ρ_m, ρ_1, ρ_2

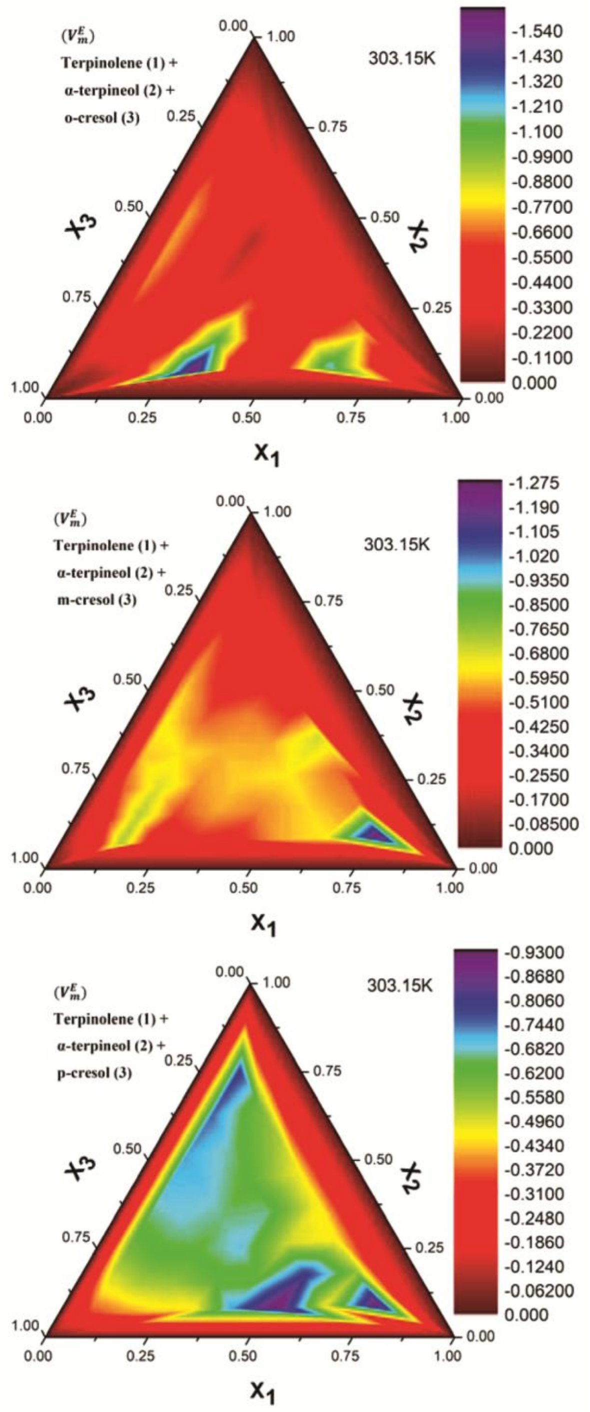

Fig. 1 — Excess molar volumes (V_m^E) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

and ρ_3 represent the densities of the ternary liquid mixture, component 1, component 2 and component 3, respectively.

All excess and deviation properties have been fitted with the Redlich-Kister[10] polynomial equation to represent excess or deviation functions for ternary mixtures:

$$Y_{ijk}^{E} = Y_{ij}^{E} + Y_{jk}^{E} + Y_{ik}^{E} + x_1 x_2 x_3 (A_{ijk} + B_{ijk} (x_2 - x3x1 + Cijkx2 - x32x12 + Dijkx2 - x33x13 + Eijkx2 - x34x14 \quad \ldots (5)$$

Here, Y^E represents excess/deviation properties, x_i denotes the mole fraction of the ith component, and A_{ijk} , B_{ijk} , C_{ijk} , D_{ijk} , E_{ijk} are fitting coefficients. The fourth-order form of the Redlich-Kister equation provides the minimum standard deviation in Y^E. The standard deviation (σ) is calculated using following relation:

$$\sigma(Y) = \left[\frac{\Sigma(Y_{exp}^{E} - Y_{cal}^{E})}{N-P}\right]^{\frac{1}{2}} \quad \ldots (6)$$

Where, Y_{exp}^{E} , Y_{cal}^{E} represent the experimental and calculated values of excess properties, respectively. N is the number of experimental points and P is the number of parameters in the Redlich-Kister equation.

Observations derived from the values of (V_m^E) in Table S2 are noteworthy:

1. All ternary mixtures exhibit negative values of V_m^E across all studied temperatures.
2. Negative values tend to become more pronounced with an increase in temperature.
3. Progressing from *o*-cresol to *p*-cresol ternary mixtures, the negativity of V_m^E intensifies.
4. In *o*-cresol ternary mixtures, the most substantial negative V_m^E values manifest within the concentration range defined by 0.25 - 0.38 mole fraction (x_1), 0.1 - 0.25 mole fraction (x_2), and 0.75 - 0.95 mole fraction (x_3).

A detailed examination of Table S2 reveals that cresol molecules exhibit robust intermolecular interactions with the terpinolene + α-terpineol cluster for the majority of compositions. For *o*-cresol and *m*-cresol-containing mixtures, the strength of these interactions increases with temperature. Conversely, in *p*-cresol-containing mixtures, the strength of interactions increases up to 308.15 K, beyond which it diminishes at higher temperatures (313.15 K) across most compositions.

The most pronounced interactions are observed in *o*-cresol-containing ternary mixtures, as evidenced by the maxima values of V_m^E listed below in Table 2.

Table 2 — Maxima values of V_m^E for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction x_1	x_2	x_3	V_m^E (cm^3·mol^{-1})
Terpinolene + α-terpineol + *o*-cresol	303.15	0.3172	0.0761	0.6067	-1.6342
	308.15	0.3172	0.0761	0.6067	-1.6483
	313.15	0.3172	0.0761	0.6067	-1.6646
Terpinolene + α-terpineol + *m*-cresol	303.15	0.7638	0.0917	0.1445	-1.2786
	308.15	0.7638	0.0917	0.1445	-1.2824
	313.15	0.7638	0.0917	0.1445	-1.2854
Terpinolene + α-terpineol + *p*-cresol	303.15	0.5217	0.0835	0.3948	-0.9344
	308.15	0.5217	0.0835	0.3948	-0.9349
	313.15	0.7638	0.0917	0.1445	-0.8632

These findings illuminate the temperature-dependent nature of intermolecular interactions within the studied ternary mixtures, offering valuable insights into the underlying molecular dynamics.

Viscosity (η), Deviation in Viscosity (Δη) and Excess Gibbs' free energy of activation of viscous flow (ΔG^{*E})

The experimentally measured viscosities (η) of pure components and their ternary mixtures, along with the calculated values of deviation in viscosities ($\Delta\eta$) and excess Gibbs' free energy of activation of viscous flow (ΔG^{*E}), are presented in Table S4. Graphical representations of $\Delta\eta$ and ΔG^{*E} *versus* mole fraction (x_1, x_2, x_3) at 303.15 K are shown in Fig. 2 and Fig. 3, respectively. The fitting coefficients $(A_{ijk}, B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk})$ of the Redlich-Kister polynomial equation for $\Delta\eta$ and ΔG^{*E} are listed in Tables S5 and S6, respectively.

The deviation in viscosity ($\Delta\eta$) and excess Gibbs' free energy for activation of viscous flow (ΔG^{*E}) are determined through the following mathematical relations:

$$\Delta\eta\ (mPa\cdot s)\ = \eta_{123} - (x_1\eta_1 + x_2\eta_2 + x_3\eta_3) \quad \ldots (7)$$

$$\Delta G^{*E}\ (J\cdot mol^{-1}) = RT\ \{\ln(\eta V) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2) - x_3 \ln(\eta_3 V_3)\} \quad \ldots (8)$$

Here, V_1, V_2, V_3, and V represent the molar volumes of components 1, 2, 3, and the mixture, respectively. Similarly, η_1, η_2, η_3, and η represent the viscosity of components 1, 2, 3, and the mixture, respectively. The universal gas constant is denoted by R, and T signifies temperature.

Observations from Table S4 include:

- All ternary mixtures exhibit negative $\Delta\eta$ values across the entire composition range and at all studied temperatures.

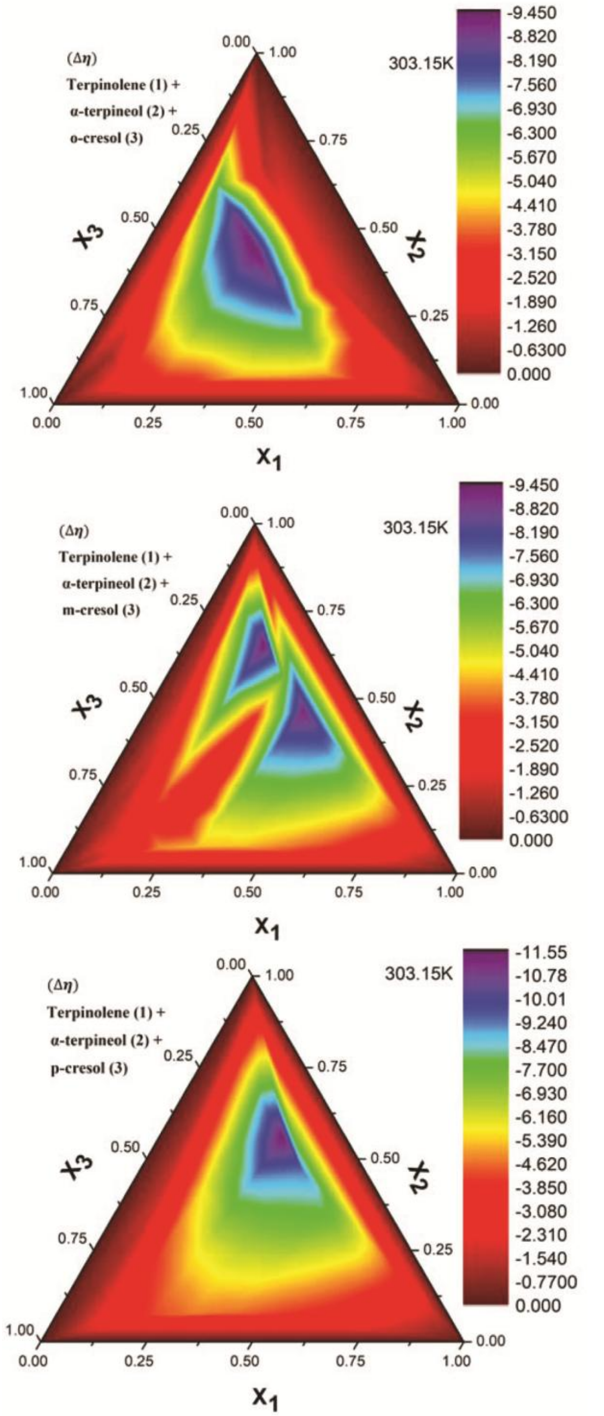

Fig. 2 — Deviation in viscosities ($\Delta\eta$) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

- The negative $\Delta\eta$ values become less negative with a rise in temperature.
- ΔG^{*E} values exhibit both positive and negative values for all ternary mixtures and at all studied temperatures.

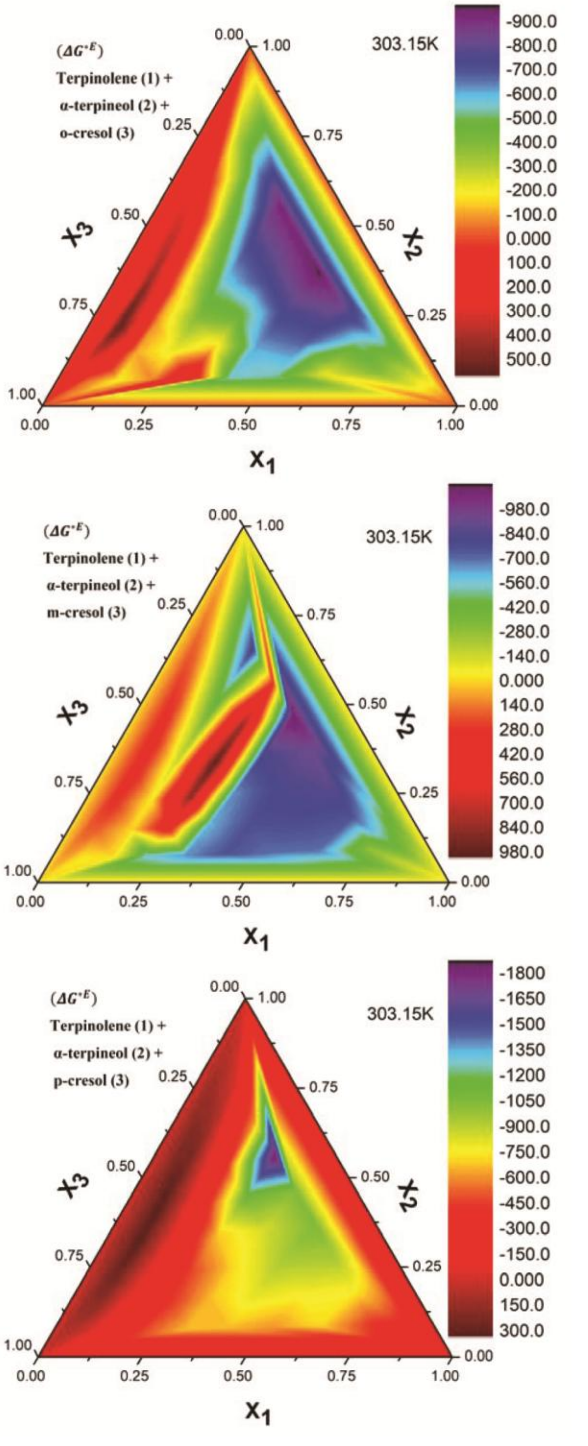

Fig. 3 — The excess Gibbs energy of activation for viscous flow (ΔG^{*E}) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

- Negative ΔG^{*E} values shift towards less negativity, while positive ΔG^{*E} values shift towards more positivity with an increase in temperature.

Table 3 — Maxima values of $\Delta\eta$ for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction x_1	x_2	x_3	$\Delta\eta$ (mPa·s)
Terpinolene + α-terpineol + *o*-cresol	303.15	0.0766	0.2205	0.7029	-0.949
	308.15	0.0766	0.2205	0.7029	-0.236
	313.15	0.0766	0.2205	0.7029	-0.043
Terpinolene + α-terpineol + *m*-cresol	303.15	0.0771	0.2221	0.7008	-1.238
	308.15	0.0806	0.3094	0.6100	-0.510
	313.15	0.0806	0.3094	0.6100	-0.150
Terpinolene + α-terpineol + *p*-cresol	303.15	0.0740	0.1420	0.7840	-1.271
	308.15	0.0806	0.3094	0.6100	-0.659
	313.15	0.0806	0.3094	0.6100	-0.252

Table 4 — Maxima of ΔG^{*E} for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction x_1	x_2	x_3	ΔG^{*E} ($J \cdot mol^{-1}$)
Terpinolene + α-terpineol + *o*-cresol	303.15	0.0766	0.2205	0.7029	560.75
	308.15	0.0766	0.2205	0.7029	589.08
	313.15	0.0766	0.2205	0.7029	583.40
Terpinolene + α-terpineol + *m*-cresol	303.15	0.2636	0.3374	0.3990	1004.05
	308.15	0.0806	0.3094	0.6100	389.88
	313.15	0.0843	0.4049	0.5108	397.77
Terpinolene + α-terpineol + *p*-cresol	303.15	0.0844	0.4049	0.5107	333.01
	308.15	0.0844	0.4049	0.5107	341.00
	313.15	0.0844	0.4049	0.5107	359.90

The maxima values of $\Delta\eta$ and ΔG^{*E} for all mixtures are given in the following Table 3 and Table 4.

As earlier discussion, if the difference of the viscosity of pure components is large. The $\Delta\eta$ values show the negative values in the case of presence of strong interactions in ternary mixtures. These $\Delta\eta$ values become more positive with increase of intermolecular interaction strength.

A perusal of Table S4 reveals that the highest intermolecular interactions between ternary mixtures' components are observed in *o*-cresol containing mixtures. The strength of intermolecular interactions increases with increase of temperature. These interactions may be of H-bonding and dipole-dipole types.

Similarly, the positive values of ΔG^{*E} also supports above discussion. Looking at the Fig. 2 and Fig. 3, they indicate that the highest strong interactions are occurring at a very low concentration of terpinolene and rich concentration of cresol molecules. These phenomena indicate that a new H-bonding is forming between α-terpineol and cresol molecules.

Refractive Index $(\mathbf{n_D})$ and Deviation in Refractive Index $(\Delta\mathbf{n_D})$

The experimentally measured refractive index (n_D) and calculated values of deviation in refractive index (Δn_D) for all ternary mixtures at various temperatures are presented in Table S7. The graphical representation of Δn_D *versus* volume fraction (ϕ_1, ϕ_2, ϕ_3) at 303.15 K for all ternary mixtures is illustrated in Fig. 4. The fitting coefficients $(A_{ijk}, B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk})$ of the Redlich-Kister polynomial equation for Δn_D are thoughtfully compiled in Table S8.

The deviation in refractive index (Δn_D) has been determined utilizing the following relations[11]:

$$\Delta n_D = n_{D_{exp}} - (n_{D_1}\phi_1 + n_{D_2}\phi_2 + n_{D_3}\phi_3) \qquad \text{... (9)}$$

$$\phi_i = \frac{x_i V_i}{\sum_{i=1}^{2} x_i V_i} \qquad \text{... (10)}$$

$$V_i = \frac{M_i}{\rho_i} \qquad \text{... (11)}$$

Here, ϕ_1, ϕ_2, ϕ_3 and $n_{D_1}, n_{D_2}, n_{D_3}$ represents the volume fraction and refractive index of component 1, 2 and 3 respectively. x_i, V_i, M_i represents mole fraction, molar volume and molar mass of ith component, respectively.

Several noteworthy observations emerge from the data presented in Table S7:

- All ternary mixtures exhibit positive values of deviation in refractive index (Δn_D) across all studied temperatures.
- The positive values of Δn_D tend to increase with a rise in temperature, although some compositions show a decrease in positive values when transitioning from 308.15 K to 313.15 K.

Maxima values of Δn_D for all mixtures are listed in Table 5.

Table 5 — maxima values of Δn_D for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction			Δn_D
		ϕ_1	ϕ_2	ϕ_3	
Terpinolene + α-terpineol + *o*-cresol	303.15	0.1000	0.3000	0.6000	0.0038
	308.15	0.1000	0.5000	0.4000	0.0030
		0.1000	0.4000	0.5000	0.0030
	313.15	0.1000	0.4000	0.5000	0.0036
		0.1000	0.3000	0.6000	0.0036
Terpinolene + α-terpineol + *m*-cresol	303.15	0.2000	0.3000	0.5000	0.0035
		0.2000	0.2000	0.6000	0.0035
	308.15	0.1000	0.1000	0.8000	0.0034
	313.15	0.1000	0.6000	0.3000	0.0059
Terpinolene + α-terpineol + *p*-cresol	303.15	0.2000	0.7000	0.1000	0.0030
	308.15	0.3000	0.1000	0.6000	0.0031
	313.15	0.2000	0.5000	0.3000	0.0040

The positive values of Δn_D suggest the presence of strong dipole-dipole or H-bonding interactions among the components of the mixtures. Such interactions enhance the polarizability of the mixture solution, resulting in positive values of Δn_D. Analyzing the

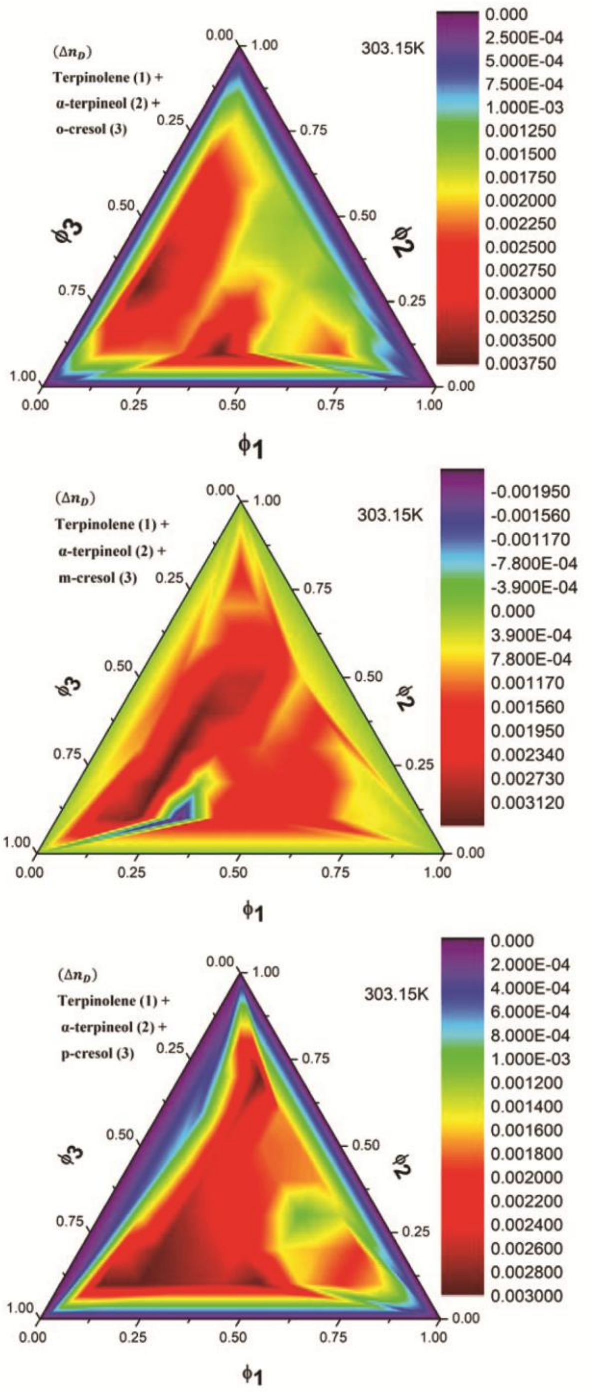

Fig. 4 — Deviation in refractive index (Δn_D) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of volume fraction at T = 303.15K.

data of Δn_D, it can be inferred that the polarizability of the mixture solution decreases with a temperature change from 303.15 K to 308.15 K. However, at a higher temperature (313.15 K), the polarizability increases.

This behavior indicates a nuanced interplay of molecular forces within the ternary mixtures, contributing to their optical properties. The observed trends in Δn_D offer valuable insights into the nature and strength of intermolecular interactions, specifically the dynamic changes in polarizability with temperature variations.

Speed of Sound ($\mathbf{u}$) and Deviation in Speed of Sound ($\mathbf{\Delta u}$)

The experimentally measured values of the speed of sound (u) and the calculated values of the deviation in speed of sound (Δu) across the entire composition range for all ternary mixtures at various temperatures are compiled in Table S9. The graphical representation of Δu *versus* mole fraction (x_1, x_2, x_3) at 303.15 K for all ternary mixtures is depicted in Fig. 5. The fitting coefficients ($A_{ijk}, B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk}$) of the Redlich-Kister polynomial equation for Δu are listed in Table S10.

The deviation in the speed of sound (Δu) has been calculated using the following relations:

$$\Delta u \; (m \cdot s^{-1}) = u_{exp} - (x_1 u_1 + x_2 u_2 + x_3 u_3) \qquad \text{... (12)}$$

Here, u_{exp} represents the speed of sound of the mixture, while x_1, x_2, x_3 and u_1, u_2, u_3 represent the mole fraction and speed of sound of pure components 1, 2 and 3, respectively.

Several insightful observations can be drawn from the values presented in Table S9:

- All ternary mixtures exhibit both positive and negative Δu values at all studied temperatures, depending on the composition ratio.
- With the rise in temperature, the positive values of Δu tend to become less positive, while the negative values of Δu become more negative for most composition ratios.

Maxima values of Δu for all mixtures are listed in Table-6.

The values of V_m^E, $\Delta\eta$ and Δn_D collectively suggest that, as ternary mixtures transition from *o*-cresol to *p*-cresol molecules, the molecules tend to orient themselves at a greater distance due to a weakening in the overall effect of various intermolecular interactions. This trend is further accentuated with an increase in temperature.

However, a contrasting trend is observed in the case of Δu values. The reversed result may be attributed to the following factors:

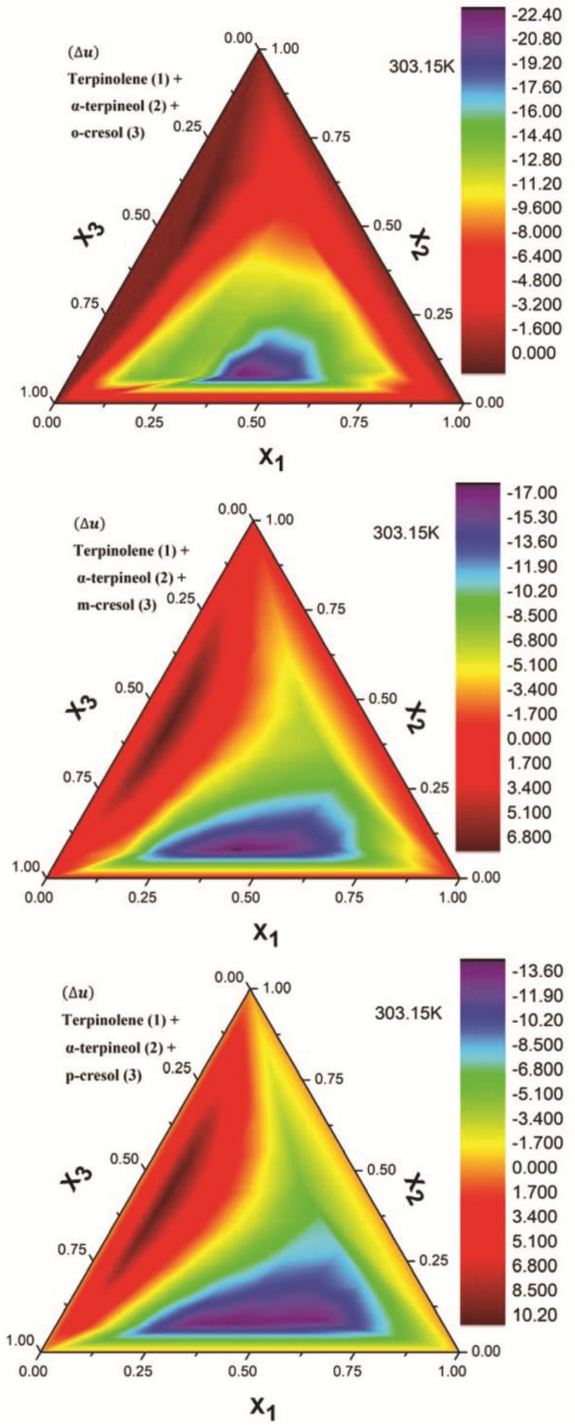

Fig. 5 — Deviation in speed of sound (Δu) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

Table 6 — Maxima values of Δu for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction x_1	x_2	x_3	Δu (m·s^{-1})
Terpinolene + α-terpineol + *o*-cresol	303.15	0.0881	0.5075	0.4044	1.30
	308.15	0.0881	0.5075	0.4044	1.08
	313.15	0.0881	0.5075	0.4044	0.76
Terpinolene + α-terpineol + *m*-cresol	303.15	0.0843	0.4049	0.5018	7.71
	308.15	0.0843	0.4049	0.5108	6.72
	313.15	0.0843	0.4049	0.5108	5.91
Terpinolene + α-terpineol + *p*-cresol	303.15	0.0844	0.4049	0.5107	10.83
	308.15	0.0844	0.4049	0.5107	9.99
	313.15	0.0844	0.4049	0.5107	9.43

- Weakening of H-bonding with an increase in temperature, as H-bonding interactions typically facilitate the easy transmission of sound waves through a liquid medium. The weakened H-bonding at higher temperatures, due to increased kinetic energy, may result in less positive or more negative values of Δu.
- Within the ternary mixture cluster, the *p*-cresol molecules might experience less steric hindrance with at least two components, facilitated by the geometric positions of the $-CH_3$ and $-OH$ groups. This factor could potentially enhance H-bonding formation, leading to higher positive values of Δu.

Isentropic Compressibility ($\mathbf{k_s}$), Deviation in Isentropic Compressibility ($\Delta\mathbf{k_s}$), Acoustical Impedance ($\mathbf{z}$), Deviation in Acoustical Impedances ($\Delta\mathbf{z}$) and Intermolecular Free Length ($\mathbf{L_f}$)

The calculated values of isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s), acoustical impedance (z), deviation in acoustical impedances (Δz), and intermolecular free length (L_f) for all ternary mixtures across the entire composition range at various temperatures are presented in Table S11, Table S13, and Table S15, respectively. The graphical representation of Δk_s, Δz and L_f *versus* mole fraction (x_1, x_2, x_3) at 303.15 K for all ternary mixtures is illustrated in Fig. 6, Fig. 7 and Fig. 8 respectively. The values of fitting coefficients ($A_{ijk}, B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk}$) of the Redlich-Kister polynomial equation for Δk_s and Δz are listed in Table S12 and S14, respectively.

These properties were calculated using the following relations[11]:

$$k_s(T\ Pa^{-1}) = \frac{1}{u_i^2\ \rho_i} \quad \text{... (13)}$$

$$Z\ (g \cdot m^{-2} \cdot s^{-1}) = u_i \rho_i \quad \text{... (14)}$$

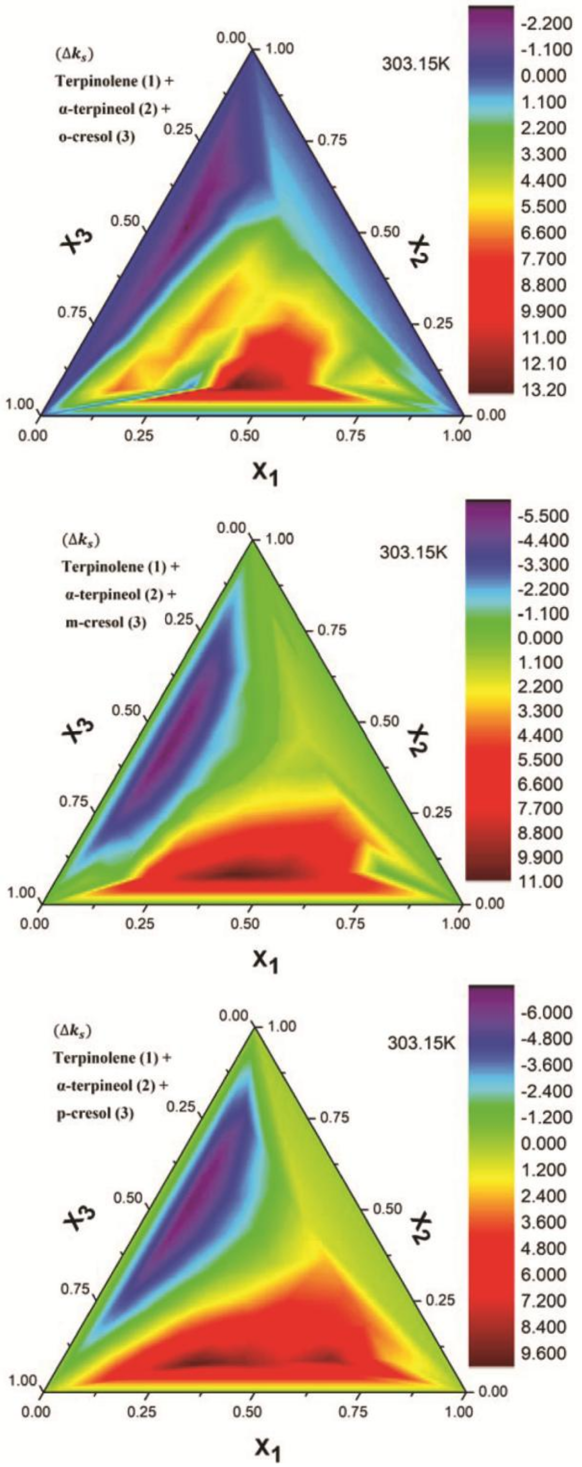

Fig. 6 — Deviation in isentropic compressibility (Δk_s) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

$$Lf = Kk_s^{1/2} \quad \text{... (15)}$$

$$\Delta k_s = k_{s_{exp}} - (x_1 k_{s_1} + x_2 k_{s_2} + x_3 k_{s_3}) \quad \text{... (16)}$$

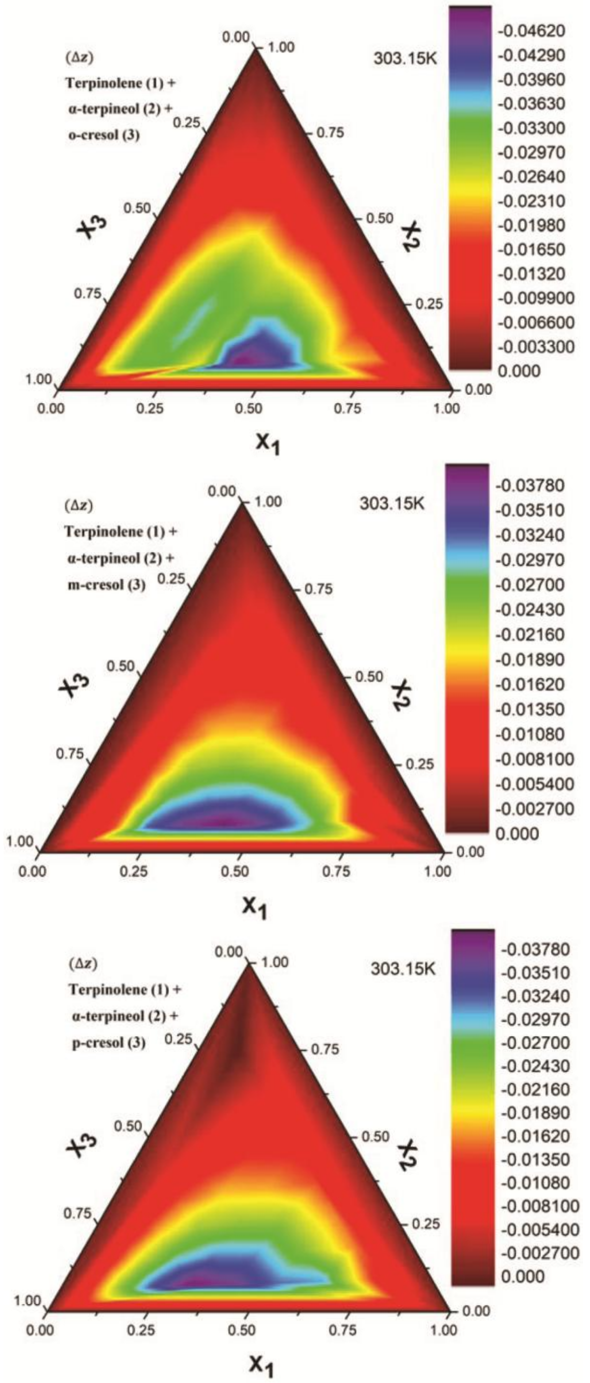

Fig. 7 — Deviation in acoustical impedance (Δz) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

$$\Delta z = z_{exp} - (x_1 z_1 + x_2 z_2 + x_3 z_3) \quad \ldots (17)$$

Here, x_1, x_2, x_3; ϕ_1, ϕ_2, ϕ_3; $k_{s_1}, k_{s_2}, k_{s_3}$ and z_1, z_2, z_3 represent mole fraction, volume fraction, isentropic compressibility, and acoustical impedance of component 1, 2, and 3 respectively. $k_{s_{exp}}$ and z_{exp} represent isentropic compressibility and acoustical impedance of ternary mixtures. u_i and ρ_i represent the speed of sound and density of ith component, respectively. K is the temperature dependent Jacobson constant.

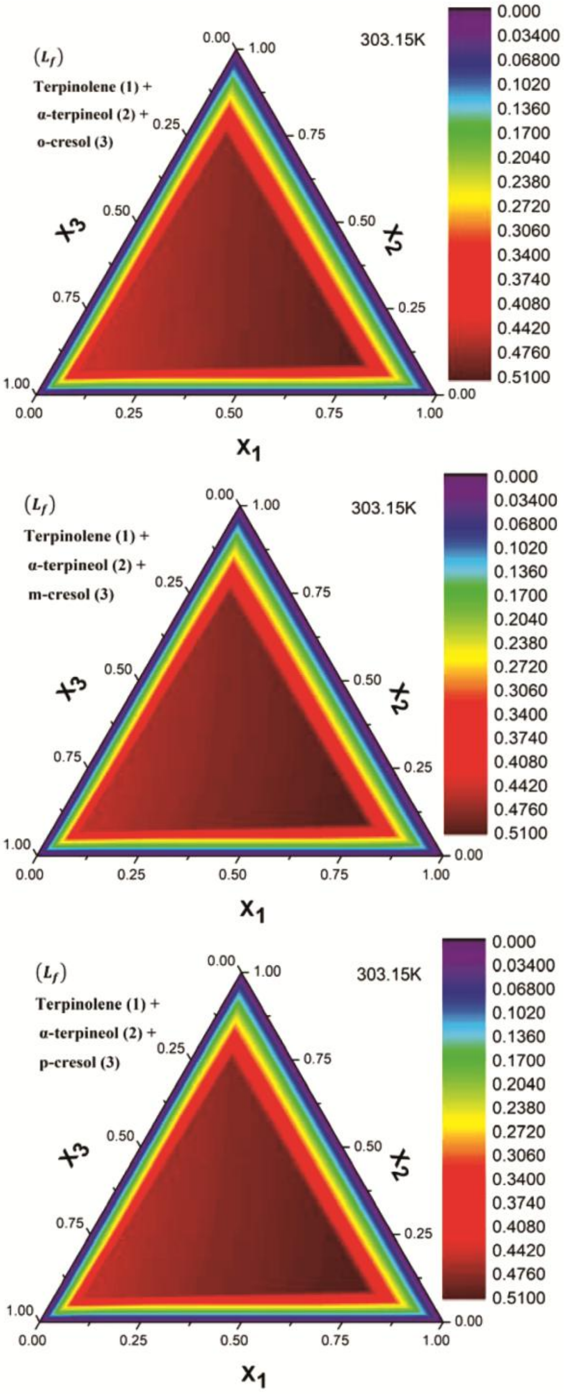

Fig. 8 — Intermolecular Free Length (L_f) for the system Terpinolene (1) α-terpineol (2) + *o*-cresol/m-cresol/p-cresol (3) as a function of mole fraction at T = 303.15K.

Several key observations can be drawn from the values of Δk_s, Δz, and L_f:

- All ternary mixtures exhibit both negative and positive values of Δk_s at all studied temperatures, reflecting diverse intermolecular interactions according to composition ratios.
- The Δz values are consistently negative for all ternary mixtures across the entire composition range at all studied temperatures.
- The L_f values become increasingly positive with the rise in temperature.

Maxima values of Δk_s and Δz for all mixtures are listed in Table 7 and Table 8.

As discussed earlier in the context of Δu, the negative values of Δk_s indicate the presence of strong intermolecular interactions between components of the mixtures. Similarly, the values of Δz and L_f also corroborate the observed trend in intermolecular interactions discussed above. These parameters collectively contribute to our understanding of the acoustical and structural aspects of the ternary mixtures, offering valuable insights into their dynamic behavior.

Table 7 — Maxima values of Δk_s for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction			Δk_s (TPa^{-1})
		x_1	x_2	x_3	
Terpinolene + α-terpineol + *o*-cresol	303.15	0.0881	0.5075	0.4044	-2.85
	308.15	0.0881	0.5075	0.4044	-2.96
	313.15	0.0881	0.5075	0.4044	-3.00
Terpinolene + α-terpineol + *m*-cresol	303.15	0.0843	0.4049	0.5108	-6.12
	308.15	0.0885	0.5096	0.4019	-5.87
	313.15	0.0885	0.5096	0.4019	-5.74
Terpinolene + α-terpineol + *p*-cresol	303.15	0.0885	0.5097	0.4018	-7.08
	308.15	0.0885	0.5097	0.4018	-7.08
	313.15	0.0885	0.5097	0.4018	-7.15

Table 8 — Maxima values of Δz for all mixtures

Ternary Mixture	Temperature (K)	Mole fraction			Δz (g·m^{-2}·s^{-1}) × 10^{-3}
		x_1	x_2	x_3	
Terpinolene + α-terpineol + *o*-cresol	303.15	0.0979	0.7522	0.1499	-0.0076
	308.15	0.0979	0.7522	0.1499	-0.0074
	313.15	0.0979	0.7522	0.1499	-0.0074
Terpinolene + α-terpineol + *m*-cresol	303.15	0.0930	0.6252	0.2818	-0.0047
	308.15	0.0981	0.7534	0.1485	-0.0048
	313.15	0.0981	0.7534	0.1485	-0.0050
Terpinolene + α-terpineol + *p*-cresol	303.15	0.0930	0.6252	0.2818	-0.0012
	308.15	0.0930	0.6252	0.2818	-0.0017
	313.15	0.0930	0.6252	0.2818	-0.0021

FT-IR Analysis

The FT-IR spectra of pure components and their ternary mixtures at various composition ratios (1:1:1, 2:1:1, 1:2:1, and 1:1:2) were recorded at 298.15 K to discern the presence of intermolecular interactions among the components of ternary mixtures (Table 9). The interpreted FT-IR spectra of ternary mixtures at different composition ratios are visually represented in Figs. S1 to S15.

The analysis focuses on five key functional groups with significant implications for intermolecular interactions. These functional groups include intermolecular H-bonding (v_{O---H}), free phenolic $-OH$ stretching (v_{O-H}), aliphatic $C-H$ symmetrical stretching (v_{C-H}), aromatic $C-H$ symmetrical stretching (v_{C-H}), and cresol's $C-O$ functional group's stretching (v_{C-O}).

The standard characteristics IR frequencies for selected functional groups are as follow: 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 $C-O$ stretching (v_{C-O})[12,13].

The observed shift values of the H-bonding frequency (v_{O---H}) concerning α-terpineol and *o*-cresol's values exhibit negativity. This negative shift indicates the formation of new H-bonding between components of ternary mixtures. It is noteworthy that the newly formed H-bond is weaker than in the pure component state of α -terpineol and *o*-cresol. Conversely, the shift values of (v_{O---H}) (H-bonding) for *m*-cresol and *p*-cresol-containing mixtures, concerning pure cresol values, are positive, suggesting that the new H-bonding is stronger than in the pure component state of *m*-cresol and *p*-cresol. The absence of the frequency of the free phenolic $-OH$ functional group in the spectra indicates a robust involvement of the $-OH$ group in intermolecular H-bonding.

Similarly, the shift values of (v_{C-H}) frequency for aliphatic and aromatic $C-H$ groups and v_{C-O} frequency also confirm their participation in intermolecular interactions. This insightful FT-IR analysis provides valuable information about the nature and strength of intermolecular interactions within the ternary mixtures at different composition ratios.

Table 9 — Experimental FT-IR and theoretical IR Frequencies with wavenumbers ($\boldsymbol{cm^{-1}}$) and shifting of bands of Terpinolene (1) + α-Terpineol (2) + *o*-, *m*- and *p*-Cresol (3) ternary mixtures at 298.15K.

Component/ Mixture		Intermolecular H-Bonded $v_{o\ldots H}$	Free Phenolic –OH Symmetrical Stretching v_{o-H}	Aliphatic C-H Symmetrical Stretching v_{C-H}	Aromatic C-H Symmetrical Stretching v_{C-H}	Aromatic ring C-X stretching v_{C-X}
Terpinolene		-	-	2909.01/2965.00	3017.40	-
α-Terpineol		3383.81	3605.62	2923.89/2965.70	3047.81/3008.93	1222.42
o-Cresol		3417.12	3778.53	2920.35	3033.00	1242.00
m-Cresol		3330.66	3755.85	2921.00	3039.40	1266.36
p-Cresol		3331.37	3779.24	2921.77	3023.81	1236.60
Terpinolene +	1:1:1	3379.56	-	2922.48 / 2966.41	- / 3012.48	- / 1245.10
α-Terpineol +	2:1:1	3378.14	-	1922.48 / 2965.70	Not Seen	- / 1241.56
o-Cresol	1:2:1	3374.60	-	2923.19 / 2966.41	- / 3010.35	- / 1245.81
Experimental	1:1:2	3379.56	-	2922.48 / 2966.41	3057.12 / 3010.02	- / 1245.10
Terpinolene +	1:1:1	3373.18	-	2923.19 / 2966.41	3039.40/ -	- / 1270.61
α-Terpineol +	2:1:1	3375.30	-	2922.48 / 2965.70	3037.28 / -	- / 1270.61
m-Cresol	1:2:1	3382.39	-	2923.89 / 2966.41	3039.40 / -	- / 1271.32
Experimental	1:1:2	3332.06	-	2921.77 / 2965.70	3039.40 / 3018.85	- / 1269.19
Terpinolene +	1:1:1	3373.89	-	2922.48 / 2966.41	- / 3013.18	1226.67 / 1240.14
α-Terpineol +	2:1:1	3383.10	-	2921.77 / 2965.70	- / 3011.77	1226.67 / -
p-Cresol	1:2:1	3373.89	-	2923.19 / 2966.41	- / 3011.06	1225.97 / 1240.14
Experimental	1:1:2	3354.75	-	2921.77 / 2966.41	- / 3015.31	1228.09 / 1240.14
Shift in wavenumber with respect to pure Terpinolene values						
Terpinolene +	1:1:1	-	-	13.47 / 1.41	- / -4.92	-
α-Terpineol +	2:1:1	-	-	13.47 / 0.70	-	-
o-Cresol	1:2:1	-	-	14.18 / 1.41	- / -7.05	-
Experimental	1:1:2	-	-	13.47 / 1.41	- / -7.38	-
Terpinolene +	1:1:1	-	-	14.18 / 1.41	- / -	-
α-Terpineol +	2:1:1	-	-	13.47 / 0.70	- / -	-
m-Cresol	1:2:1	-	-	14.88 / 1.41	- / -	-
Experimental	1:1:2	-	-	12.76 / 0.70	- / 1.45	-
Terpinolene +	1:1:1	-	-	13.47 / 1.41	- / -4.22	-
α-Terpineol +	2:1:1	-	-	12.76 / 0.70	- / -5.63	-
p-Cresol	1:2:1	-	-	14.18 / 1.41	- / -6.34	-
Experimental	1:1:2	-	-	12.76 / 1.41	- / -2.09	-
Shift in wavenumber with respect to pure α-Terpineol values						
Terpinolene +	1:1:1	-4.25	-	-1.41 / 0.71	- / 3.55	-
α-Terpineol +	2:1:1	-5.67	-	-1.41 / 0	-	-
o-Cresol	1:2:1	-9.21	-	-0.7 / 0.71	- / 1.42	-
Experimental	1:1:2	-4.25	-	-1.41 / 0.71	9.31 / 1.09	-
Terpinolene +	1:1:1	-10.63	-	-0.70 / 0.71	-8.41 / -	-
α-Terpineol +	2:1:1	-8.51	-	-1.41 / 0	-10.53 / -	-
m-Cresol	1:2:1	-1.42	-	- / 0.71	-8.41 / -	-
Experimental	1:1:2	-51.75	-	-2.12 / 0	-8.41 / 9.92	-
Terpinolene +	1:1:1	-9.92	-	-1.41 / 0.71	- / 4.25	4.25 / -
α-Terpineol +	2:1:1	-0.71	-	-2.12 / 0	- / 2.84	4.25 / -
p-Cresol	1:2:1	-9.92	-	-0.70 / 0.71	- / 2.13	3.55 / -
Experimental	1:1:2	-29.06	-	-2.12 / 0.71	- / 6.38	5.67 / -
Shift in wavenumber with respect to pure Cresol values						
Terpinolene +	1:1:1	-37.56	-	2.13 / -	-	3.10
α-Terpineol +	2:1:1	-38.98	-	2.13 / -	-	-0.44
o-Cresol	1:2:1	-42.52	-	2.84 / -	-	3.81
Experimental	1:1:2	-37.56	-	2.13 / -	24.12	3.1
Terpinolene +	1:1:1	42.52	-	2.19 / -	0	4.25
α-Terpineol +	2:1:1	44.64	-	1.48 / -	-2.12	4.25
m-Cresol	1:2:1	51.73	-	2.89 / -	0	4.96
Experimental	1:1:2	1.40	-	0.77 / -	0	2.83

(*Contd.*)

Table 9 — Experimental FT-IR and theoretical IR Frequencies with wavenumbers (cm^{-1}) and shifting of bands of Terpinolene (1) + α-Terpineol (2) + *o*-, *m*- and *p*-Cresol (3) ternary mixtures at 298.15K. (*Contd.*)

Component/ Mixture		Intermolecular H-Bonded $v_{o\dots H}$	Free Phenolic –OH Symmetrical Stretching v_{o-H}	Aliphatic C-H Symmetrical Stretching v_{C-H}	Aromatic C-H Symmetrical Stretching v_{C-H}	Aromatic ring C-X stretching v_{C-X}
Terpinolene +	1:1:1	42.52	-	0.71 / -	-	3.54
α-Terpineol +	2:1:1	51.73	-	0 / -	-	-
p-Cresol	1:2:1	42.52	-	1.42 / -	-	3.54
Experimental	1:1:2	23.38	-	0 / -	-	3.54

The Standard Uncertainty u is u(T) = 0.1K. All spectra are taken at atmospheric pressure and composition of ternary mixture is 1:1:1, 2:1:1, 1:2:1, and 1:1:2.

Conclusion

The culmination of this research reveals critical insights into the ternary mixtures of Terpinolene, α-Terpineol, and Cresols, offering a comprehensive understanding of their intermolecular interactions. Key findings and conclusions include:

The analysis of excess properties demonstrates the unequivocal presence of robust intermolecular interactions among the components of ternary mixtures. This substantiates the intricate nature of molecular associations within the system.

A noteworthy observation is the positive correlation between temperature and the strength of intermolecular interactions. This trend is prevalent across most composition ratios, indicating an enhancement in interaction strength with a rise in temperature.

The excess properties values suggest that the most pronounced intermolecular interactions occur at composition ratios characterized by minimal concentrations of terpinolene molecules juxtaposed with elevated concentrations of cresol molecules.

The FT-IR spectra analysis provides crucial evidence supporting the formation of novel hydrogen bonding between the components of ternary mixtures. The strength of these newly formed hydrogen bonds is found to be weaker than those in pure α-terpineol and *o*-cresol but stronger than in the pure liquid state of *m*-cresol and *p*-cresol molecules.

The shift values of the v_{O---H} frequency underscore the nuanced strength of newly formed hydrogen bonds. The weaker strength in comparison to pure components like α-terpineol and *o*-cresol contrasts with the stronger bonding observed in comparison to the pure liquid state of *m*-cresol and *p*-cresol molecules.

While excess properties affirm the presence of intermolecular interactions in ternary mixtures, they do not align with the interaction order observed in the relevant terpinolene + cresols and α-terpineol + cresols binaries[1,2]. Notably, the strongest interactions are observed in *p*-cresol-containing ternaries, possibly attributable to the geometrically aligned structure of *p*-cresol, which exhibits reduced steric hindrance.

In summary, this research provides valuable insights into the complex interplay of molecules within ternary mixtures, shedding light on the temperature and composition-dependent nature of intermolecular interactions. The findings contribute to the broader understanding of molecular behavior in multi-component systems.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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