International Journal of Chemistry Studies
www.chemistryjournal.in
ISSN: 2581-348X
Received: 04-01-2026, Accepted: 04-02-2026, Published: 21-02-2026
Volume 10, Issue 1, 2026, Page No. 26-37

# Study of solute-solvent interactions of Isopropyl benzene (cumene) with aromatic hydrocarbons at temperature 298.15 K: A viscometric approach

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**Abstract**

A study on thermodynamic parameters of liquids plays an important role for chemical engineering field. The thermodynamic and transport properties of isopropyl benzene (cumene) and aromatic hydrocarbons binary mixture were studied for temperature 298.15 K. The density, viscosity, sound velocity, compressibility, etc are calculated and the results are fitted to Redlich- Kister polynomial equation. The molecular interaction for the binary mixture was explained using the calculated data. Experimental densities (ρ), viscosities (η), and sound velocities (u) were measured at 298.15 K and atmospheric pressure for binary liquid mixtures of isopropyl benzene (cumene) with ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl. Based on these experimental results, various thermodynamic excess functions and deviation properties were subsequently evaluated. Physical properties such as density, viscosity and speed of sound, play a crucial role in determining the excess thermodynamic properties of chemical mixtures. These properties provide valuable insight into molecular interactions and help predict the behavior of complex chemical systems. The research offers fresh experimental data, and the findings show that the binary systems of isopropyl benzene (cumene) with the aromatic hydrocarbons under investigation (ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl) have comparatively weak intermolecular interactions.

**Keywords:** Density, viscosity, speed of sound, excess properties, excess free volume, excess enthalpy, Cumene, binary systems, aromatic hydrocarbon

## Introduction

Liquid phase is the intermediate phase between a solid and the gas phase. A solution is a homogeneous mixture of two or more liquids. A liquid mixture is obtained by mixing two, three or four homogeneous liquids called binary, ternary and quaternary liquid mixtures respectively. Based on Raoult's law liquid solutions are classified into two called real and ideal solutions. The interactions occurring between the molecules of liquid mixtures results in deviation from the ideal behaviour of liquid mixture [1]. The thermodynamic properties are useful in understanding the nature of interactions occurring between the molecules in liquid mixtures. Thermodynamic and transport properties of pure liquids as well as liquid mixtures plays vital role in various fields such as textile, oil, pharmaceutical, chemicals etc [2-5]. The measurements of density, viscosity, ultrasonic velocity and other thermodynamic parameters of liquid mixtures clearly explain the nature of interaction between the like and unlike molecules. Strong or weak interactions between unlike molecules in a mixture often result in deviations from ideal behaviour. Such deviations in binary liquid mixtures are typically linked to synergistic effects arising from differences in the molecular structure and chemical nature of the constituent solvents [6–8], as well as external factors such as temperature and composition. Molecular interactions within these systems play a critical role in determining their overall chemical behaviour. Physical properties—including refractive index, speed of sound, viscosity, and density are commonly measured to characterise these interactions and to provide insight into the underlying molecular forces at play [9, 10]. These physical properties can be used to calculate various excess thermodynamic functions, including free volume, internal pressure, and isentropic compressibility, among others. Information about solvent structure and interactions can be inferred from these properties and their derived quantities [11]. Accurate Thermophysical data for binary systems are of primary importance in the design and optimization of industrial processes. Such properties are essential not only for a fundamental understanding of mixing behaviour, but also for addressing practical challenges encountered in the development of products, processes, and equipment. Excess properties defined as deviations from ideal-solution behaviour are particularly valuable for verifying and developing theoretical models of dissolution and molecular interactions [12]. Excess properties quantify the extent of non-ideality in liquid mixtures and arise from molecular association or other specific intermolecular interactions. A variety of forces may act between unlike molecules, including dispersion forces, charge-transfer interactions, hydrogen bonding, and dipole–dipole or dipole–induced-dipole interactions. In many systems, more than one type of interaction operates simultaneously. Dispersion forces present in all mixtures generally contribute positively to excess values, whereas charge-transfer interactions, dipole–induced-dipole interactions, dipole–dipole interactions, and hydrogen bonding typically contribute negatively. The relative magnitude of these contributions depends on both the nature of the components and the mixture composition. Furthermore, dissociation of a component that is associated

in its pure state tends to yield positive excess values. A transition from positive to increasingly negative excess values indicates strengthening interactions between unlike molecules, which may be interpreted qualitatively as a closer approach of the molecules, leading to reductions in both compressibility and molar volume. Ultrasonic velocity measurements have been widely used to probe such molecular interactions in liquid mixtures. Although both spectroscopic and non-spectroscopic techniques can be used to study intermolecular behaviour, ultrasonic velocity and viscosity measurements remain among the most effective tools for evaluating interaction strength and structural characteristics of liquid systems. Internal pressure and free volume have attracted considerable interest among chemists, physicists, and chemical engineers because they provide valuable insight into molecular interactions, internal structure, clustering phenomena, and dipolar interactions within liquids and liquid mixtures. In recent years, these parameters have continued to be subjects of active research, as they play an important role in elucidating the behaviour of complex fluid systems. Numerous investigators have made significant efforts to evaluate internal pressure theoretically for both pure liquids and their mixtures, using various thermodynamic and acoustic approaches.

Fundamental thermodynamic and thermo physical properties provide essential information for understanding the non-ideal behaviour of complex liquid systems, as such behaviour arises from physical and chemical effects due to molecular interactions and intermolecular forces between unlike molecules. To examine these interactions, we report ultrasonic velocity (u), density (ρ), refractive index (n), and viscosity (η) for binary liquid mixtures of isopropyl benzene (cumene) with selected aromatic hydrocarbons over the entire composition range at 298.15 K. The experimental values of u, ρ, and η were used to evaluate adiabatic compressibility ($\beta_{ad}$), enthalpy (H) and free volume ($V_f$) their corresponding excess functions. These parameters are highly sensitive to the strength and nature of intermolecular interactions in the mixtures, and their dependence on composition provides valuable insight into the extent and type of interactions occurring between the component molecules.

## Experimental procedure

**Chemical:** The chemicals used in this study, along with their suppliers, are listed in Table 1. All chemicals possessed high purity; therefore, no additional purification procedures were undertaken. The purity of each chemical was further verified by measuring key physical properties ultrasonic velocity (u), density (ρ), refractive index (n), and viscosity (η) and comparing the results with corresponding literature values. These comparisons, presented in Table 2, show excellent agreement, confirming the reliability and suitability of the chemicals for the experimental work.

**Table 1:** The details of the chemicals used, including their CAS Registry Numbers and mass fraction purities, are provided in Table 1

| Component | Formula | CAS Reg. No. | Supplier | Mass Fraction Purity (%) | Water Content | Method Purity analysis method |
|---|---|---|---|---|---|---|
| Cumene | $C_9H_{12}$ | 80-15-9 | CDH, (P) Ltd. New Delhi, India | 99.0% | 0.1% | Double distillation |
| Mesitylene | $C_9H_{12}$ | 108-67-8 | CDH, (P) Ltd. New Delhi, India | 98.0% | 0.01% | Double distillation |
| Ethyl benzene | $C_8H_{10}$ | 100-41-4 | CDH, (P) Ltd. New Delhi, India | 98.0% | 0.1% | Double distillation |
| Toluene | $C_7H_8$ | 108-88-3 | CDH, (P) Ltd. New Delhi, India | 99.0% | 0.1% | Double distillation |
| n-Propyl benzene | $C_9H_{12}$ | 103-65-1 | CDH, (P) Ltd. New Delhi, India | 98.0% | 0.01% | Double distillation |
| t-Butyl benzene | $C_{10}H_{14}$ | 98-06-6 | CDH, (P) Ltd. New Delhi, India | 99.0% | 0.1% | Double distillation |
| Biphenyl | $C_{12}H_{10}$ | 92-52-4 | CDH, (P) Ltd. New Delhi, India | 99.0% | 0.05% | Double distillation |

**Measurements:** Six binary systems were studied: isopropyl benzene (cumene) + ethylbenzene, isopropyl benzene (cumene) + toluene, isopropyl benzene (cumene) + mesitylene, isopropyl benzene (cumene) + n-propylbenzene, isopropyl benzene (cumene) + tert-butylbenzene, and isopropyl benzene (cumene) + biphenyl. All chemicals were stored over sodium hydroxide pellets for several days and fractionally distilled twice, following the procedure reported in the literature [13]. The purification method described by Zhao *et al*. [14] was also adopted: for example, ethyl acetate was dried over $K_2CO_3$, filtered, and distilled, with the initial and final fractions discarded. All purified chemicals were stored in dark bottles over freshly activated molecular sieves to minimize moisture adsorption. Each sample mixture was prepared gravimetrically by mixing accurately calculated masses of the pure components in specially designed glass-stoppered bottles. Binary mixtures covering the entire mole fraction range were prepared by injecting the required amounts of each component into sealed glass vials using gas-tight syringes to minimize evaporation losses. The pure liquids were weighed using a digital electronic balance (Citizen Scale (I) Pvt. Ltd., Mumbai, India) with a precision of ±0.1 mg, and the overall uncertainty in mole fraction was estimated to be within ±0.0005. For each binary system, five mixture compositions were prepared, and measurements of density, viscosity, and ultrasonic velocity were carried out on the same day in order to minimize compositional and environmental variations.

**Density:** Densities of the pure liquids and their binary mixtures were determined using a 25 cm³ relative density (R.D.) bottle. The bottle containing the sample was immersed in a thermostated water bath to maintain thermal stability, which was monitored using a calibrated thermometer under equilibrium conditions. Calibration of the R.D. bottle at 298.15 K was performed using triply distilled water and purified methanol, with density values taken from the literature. Conductivity water (specific conductance less than $1\times10^6$ $ohm^{-1}$) was used to verify the calibration, assuming densities of 0.9970 and 0.9940 g $cm^{-3}$ at 298.15 K, respectively. Before each measurement, the R.D. bottle was filled with bubble-free liquid and placed in a thermo stated water bath (MSI Goyal Scientific, Meerut, India) to ensure proper thermal equilibration. The uncertainty in the density measurements was found to be less than ±0.0004 g.$cm^{-3}$.

**Sound velocity:** Ultrasonic velocities were measured using a multi-frequency ultrasonic interferometer (Model F80D, Mittal Enterprise, New Delhi, India) operating at a fixed frequency of 3 MHz. The instrument was calibrated at 298.15 K using water, methanol, and benzene. The measurement technique, described in detail elsewhere, is based on the accurate determination of the wavelength of ultrasonic waves of known frequency generated by a quartz crystal inside the measuring cell. The interferometer cell was filled with the test liquid, and a constant-temperature water bath was used to circulate water around the cell to maintain thermal stability. The uncertainty in speed of sound was estimated to be ± 1m.s$^{-1}$. The ultrasonic velocities measured for pure isopropyl benzene (cumene), ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl were found to be in good agreement with literature values. The ultrasonic velocity (U) was calculated using the following formula:

$$U = \lambda . f \quad (1)$$

**Viscosity:** The viscosities of the pure liquids and their binary mixtures were measured using a suspended Ostwald viscometer with a capacity of approximately 15 mL, a capillary length of about 90 mm, and an internal diameter of 0.5 mm. The viscometer was calibrated at 298.15 K using triply distilled water, methanol, and benzene, following standard procedures reported in the literature. The efflux time of each sample was measured with an electronic stopwatch (Racer) with a resolution of ±0.015 s, and the average of at least four consistent flow-time readings was used for each determination. A glass stopper was placed at the viscometer opening during measurements to minimise evaporation losses. The instrument's design, with two reservoir bulbs connected by a U-shaped capillary, ensures free liquid flow under atmospheric pressure. The viscosity (η) of the pure liquids and their binary mixtures was calculated using the standard viscometric relation based on measured flow times and calibrated constants.

$$\frac{\eta}{\rho} = \text{at} - \frac{b}{t} \quad (2)$$

Where t is the efflux time and a and b are viscometric constants.

The measured viscosities with an uncertainty of ±0.008 mPa.s. The viscosity values obtained for pure isopropyl benzene (cumene), ethyl benzene, toluene, mesitylene, n-propyl benzene, tert-butyl benzene, and biphenyl were found to be in good agreement with literature data.

**Table 2:** Comparison of Experimental and Literature Values of Density (ρ), Sound Velocity (u), and Viscosity (η) for Pure Components at 298.15 K and Atmospheric Pressure.

| Compound | ρ (g.cm$^{-3}$) | | u (m.s$^{-1}$) | | η (m Pa s) | |
|---|---|---|---|---|---|---|
| | Observed | Literature | Observed | Literature | Observed | Literature |
| Cumene | 0.8532 | 0.8581[26] | 1326 | 1325[31] | 0.7337 | 0.7337[26] |
| | | 0.5574[27] | | 1308[35] | | 0.7390[27] |
| Mesitylene | 0.8616 | 0.8612[23] | 1338 | 1336[23] | 0.6449 | 0.6486[32] |
| | | 0.8611[24] | | 1336[25] | | 0.6600[37] |
| Ethyl benzene | 0.8674 | 0.8620[16] | 1324 | 1312[16] | 0.6345 | 0.6280[16] |
| | | 0.8626[17] | | 1318[36] | | 0.6373[16] |
| Toluene | 0.8576 | 0.8624[15] | 1306 | 1307[19] | 0.5527 | 0.5525[21] |
| | | 0.8622[18] | | 1309[20] | | 0.5531[22] |
| n-Propyl benzene | 0.8624 | 0.8577[28] | 1315 | 1320[33] | 0.7931 | 0.7995[30] |
| | | 0.8577[29] | | 1320[34] | | 0.7827[28] |
| t-butyl benzene | 0.8624 | 0.8624[24] | 1316 | 1315[23] | 0.7449 | NA |
| | | 0.8622[23] | | 1315[25] | | NA |
| Biphenyl | 0.7920 | NA | 1118 | NA | 0.6108 | NA |

**NA:** Data not available.

## Modelling

Redlich-Kister equation The Redlich–Kister (RK) equation [38] is a widely used algebraic expression for correlating the excess properties of chemical mixtures. It expresses the excess property $Y^E$ as a function of the mole fractions ($x_1$ and $x_2$) of the components. The Redlich–Kister (RK) equation is given by:

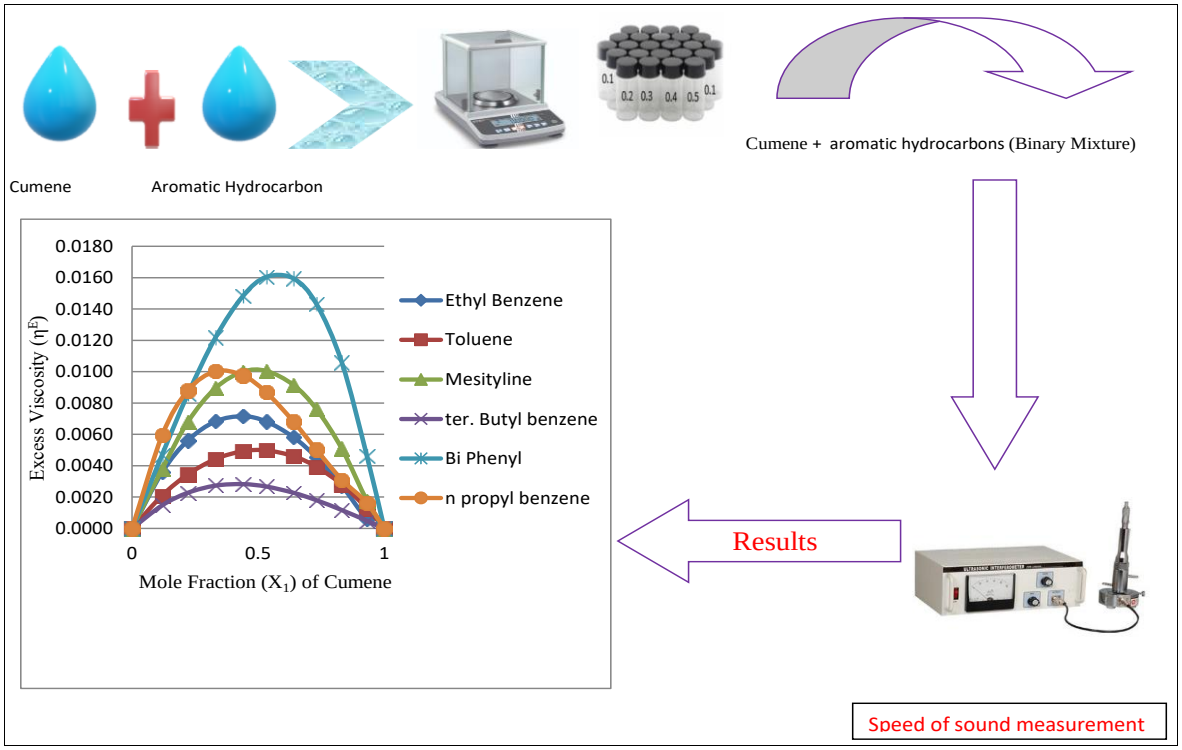
$$Y = x_1 x_2 \sum_{j=1}^{p} A_{j-1}(x_1 - x_2)^{j-1} \quad (3)$$

Where $Y$ is $(\beta_{ad}^E, n^E, V_f^E, p_i^E \text{ and } H^E)$ and $x_1$ and $x_2$ are the mole fractions of pure components 1 and 2, respectively. $a_{j-1}$ is the polynomial coefficient, and $p$ is the polynomial degree.

The goodness of fit of the regression is evaluated using statistical indicators, such as the standard deviation, which reflect the accuracy and reliability of the correlation.

## Results and Discussion

The experimental values of ultrasonic velocity (u), density (ρ), viscosity (η), and refractive index (n) for binary mixtures of isopropyl benzene (cumene) with ethyl benzene, mesitylene, n-propyl benzene, tert-butyl benzene, and biphenyl at 298.15 K are summarized in Table 3. Using these measured values, various derived thermodynamic parameters—including adiabatic compressibility $(\beta_{ad})$, enthalpy (H), and free volume ($V_f$) were calculated and are also presented in Table 3.




**Scheme 1:** Interactions between Isopropyl Benzene (Cumene) with Aromatic Hydrocarbons at 298.15K

**Table 3:** Density (ρ), Sound Velocity (u), Viscosity (η) and calculated parameters adiabatic compressibility $(\beta_{ad})$, Free Volume ($V_f$) Enthalpy (H) of Binary Mixtures of Isopropyl Benzene with Aromatic Hydrocarbons at 298.15 K

| Mole fraction Cumene ($x_1$) | Density (ρ) g.cm$^{-3}$ | Viscosity ($\eta$) mPa.s | Speed of Sound (u) ms$^{-1}$ | Adiabatic compressibility $(\beta_{ad})$ × 10$^{-7}$ Pa$^{-1}$ | Free Volume $V_f$ × 10$^{-7}$ M$^3$mol$^{-1}$ | Enthalpy (H) × 10$^{-6}$ (J.mol$^{-1}$) |
|---|---|---|---|---|---|---|
| isopropyl benzene + ethyl benzene | | | | | | |
| 0.0000 | 0.8630 | 0.6345 | 1308 | 0.6773 | 0.3512 | 3.4463 |
| 0.1193 | 0.8612 | 0.6472 | 1310 | 0.6763 | 0.3526 | 3.4737 |
| 0.2209 | 0.8600 | 0.6633 | 1314 | 0.6758 | 0.3537 | 3.4973 |
| 0.3312 | 0.8596 | 0.6715 | 1316 | 0.6751 | 0.3549 | 3.5202 |
| 0.4397 | 0.8592 | 0.3882 | 1317 | 0.6745 | 0.3561 | 3.5438 |
| 0.5319 | 0.8588 | 0.6931 | 1318 | 0.6739 | 0.3571 | 3.5610 |
| 0.6395 | 0.858 | 0.7042 | 1320 | 0.6721 | 0.3582 | 3.5794 |
| 0.7301 | 0.8572 | 0.7124 | 1321 | 0.6709 | 0.3591 | 3.5908 |
| 0.8315 | 0.8564 | 0.7198 | 1322 | 0.6694 | 0.3601 | 3.6018 |
| 0.9313 | 0.8554 | 0.7249 | 1324 | 0.6681 | 0.3611 | 3.6137 |
| 1.0000 | 0.8532 | 0.7337 | 1326 | 0.6666 | 0.3616 | 3.6191 |
| isopropyl benzene + toluene | | | | | | |
| 0.0000 | 0.8672 | 0.5527 | 1312 | 0.6699 | 0.3462 | 3.3313 |
| 0.1193 | 0.8628 | 0.5801 | 1314 | 0.6697 | 0.3481 | 3.3875 |
| 0.2209 | 0.8612 | 0.6046 | 1315 | 0.6695 | 0.3498 | 3.4302 |
| 0.3312 | 0.8600 | 0.6293 | 1316 | 0.6693 | 0.3516 | 3.4725 |
| 0.4397 | 0.8592 | 0.6457 | 1318 | 0.6691 | 0.3534 | 3.5100 |
| 0.5319 | 0.8584 | 0.6706 | 1390 | 0.6690 | 0.3548 | 3.5375 |
| 0.6395 | 0.8576 | 0.6869 | 1320 | 0.6686 | 0.3564 | 3.5643 |
| 0.7301 | 0.8568 | 0.7032 | 1321 | 0.6682 | 0.3577 | 3.5824 |
| 0.8315 | 0.8556 | 0.7191 | 1322 | 0.6677 | 0.3592 | 3.5998 |
| 0.9313 | 0.8544 | 0.7266 | 1324 | 0.6671 | 0.3606 | 3.6130 |
| 1.0000 | 0.8532 | 0.7337 | 1326 | 0.6666 | 0.3616 | 3.6191 |
| isopropyl benzene + meistylene | | | | | | |
| 0.0000 | 0.8616 | 0.6449 | 1338 | 0.6483 | 0.4753 | 3.2715 |
| 0.1193 | 0.8612 | 0.6216 | 1336 | 0.6509 | 0.4698 | 3.3161 |
| 0.2209 | 0.8608 | 0.6384 | 1335 | 0.6530 | 0.4618 | 3.3527 |
| 0.3312 | 0.8604 | 0.6551 | 1334 | 0.6552 | 0.4546 | 3.3913 |
| 0.4397 | 0.86 | 0.6718 | 1333 | 0.6574 | 0.4486 | 3.4302 |
| 0.5319 | 0.8596 | 0.6885 | 1332 | 0.6591 | 0.4356 | 3.4633 |
| 0.6395 | 0.8592 | 0.6967 | 1331 | 0.6608 | 0.4216 | 3.4999 |
| 0.7301 | 0.8588 | 0.7048 | 1330 | 0.6626 | 0.4085 | 3.5304 |
| 0.8315 | 0.8584 | 0.7130 | 1329 | 0.6643 | 0.3942 | 3.5647 |
| 0.9313 | 0.8576 | 0.7293 | 1328 | 0.6658 | 0.3751 | 3.5985 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 1.0000 | 0.8532 | 0.7337 | 1326 | 0.6666 | 0.3616 | 3.6191 |
| isopropyl benzene + n-propyl benzene | | | | | | |
| 0.0000 | 0.8624 | 0.7931 | 1315 | 0.6706 | 0.3167 | 3.7622 |
| 0.1193 | 0.8620 | 0.7896 | 1316 | 0.6703 | 0.3236 | 3.7483 |
| 0.2209 | 0.8618 | 0.7884 | 1317 | 0.6700 | 0.3298 | 3.7363 |
| 0.3312 | 0.8614 | 0.7724 | 1318 | 0.6669 | 0.3361 | 3.7230 |
| 0.4397 | 0.8604 | 0.7664 | 1319 | 0.6694 | 0.3417 | 3.7090 |
| 0.5319 | 0.8596 | 0.7626 | 1320 | 0.6692 | 0.3462 | 3.6976 |
| 0.6395 | 0.8588 | 0.7558 | 1321 | 0.6686 | 0.3508 | 3.6788 |
| 0.7301 | 0.8584 | 0.7524 | 1322 | 0.6681 | 0.3544 | 3.6634 |
| 0.8315 | 0.8576 | 0.74630 | 1324 | 0.6676 | 0.3578 | 3.6474 |
| 0.9313 | 0.8560 | 0.7422 | 1325 | 0.6669 | 0.3602 | 3.6323 |
| 1.0000 | 0.8532 | 0.7337 | 1326 | 0.6666 | 0.3616 | 3.6191 |
| isopropyl benzene + t-butyl benzene | | | | | | |
| 0.0000 | 0.8624 | 0.7449 | 1316 | 0.6695 | 0.4105 | 3.5665 |
| 0.1193 | 0.8620 | 0.7445 | 1317 | 0.6699 | 0.4055 | 3.5798 |
| 0.2209 | 0.8612 | 0.7440 | 1318 | 0.6690 | 0.4012 | 3.5895 |
| 0.3312 | 0.8604 | 0.7436 | 1390 | 0.6691 | 0.3978 | 3.5986 |
| 0.4397 | 0.8596 | 0.7420 | 1320 | 0.6689 | 0.3946 | 3.6066 |
| 0.5319 | 0.8586 | 0.7398 | 1321 | 0.6684 | 0.3906 | 3.6136 |
| 0.6395 | 0.8572 | 0.7389 | 1322 | 0.6680 | 0.3846 | 3.6164 |
| 0.7301 | 0.8564 | 0.7373 | 1323 | 0.6677 | 0.3788 | 3.6185 |
| 0.8315 | 0.8556 | 0.7364 | 1324 | 0.6673 | 0.3722 | 3.6206 |
| 0.9313 | 0.8548 | 0.7351 | 1325 | 0.6669 | 0.3656 | 3.6215 |
| 1.0000 | 0.8532 | 0.7337 | 1326 | 0.6666 | 0.3616 | 3.6191 |
| isopropyl benzene + Biphenyl | | | | | | |
| 0.0000 | 0.7920 | 0.6108 | 1118 | 0.9989 | 0.6809 | 2.9829 |
| 0.1193 | 0.7956 | 0.6215 | 1144 | 0.9694 | 0.6498 | 3.0951 |
| 0.2209 | 0.8036 | 0.6357 | 1174 | 0.9347 | 0.6314 | 3.1839 |
| 0.3312 | 0.8084 | 0.6510 | 1186 | 0.8970 | 0.6124 | 3.2722 |
| 0.4397 | 0.8144 | 0.6710 | 1198 | 0.8600 | 0.5875 | 3.3516 |
| 0.5319 | 0.8248 | 0.6932 | 1212 | 0.8281 | 0.5576 | 3.4120 |
| 0.6395 | 0.8276 | 0.7308 | 1242 | 0.7910 | 0.5202 | 3.4725 |
| 0.7301 | 0.8324 | 0.7161 | 1274 | 0.7597 | 0.4827 | 3.5183 |
| 0.8315 | 0.8436 | 0.7215 | 1286 | 0.7248 | 0.4428 | 3.5623 |
| 0.9313 | 0.8484 | 0.7295 | 1300 | 0.6904 | 0.4006 | 3.5997 |
| 1.0000 | 0.8532 | 0.7337 | 1326 | 0.6666 | 0.3616 | 3.6191 |

**Table 4:** Excess thermodynamic parameters $(\beta_{ad}^{E}, V_f^{E},$ and $H^E)$ for binary mixture of isopropyl benzene (1) + aromatic hydrocarbons (2) at 298.15K

| **Mole fraction 1,3-Dioxolane ($x_1$)** | **Excess adiabatic compressibility $\beta_{ad}^{E}$ × $10^{-7}$/ $Pa^{-1}$** | **Excess Free Volume $V_f^E$ × $10^{-7}$ $M^3mol^{-1}$** | **Excess Enthalpy $H^E$ × $10^{-4}$ ($J.mol^{-1}$)** |
|---|---|---|---|
| isopropyl benzene + ethyl benzene | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1193 | 0.0006 | 0.0123 | 0.6857 |
| 0.2209 | 0.0010 | 0.0206 | 1.2822 |
| 0.3312 | 0.0014 | 0.0281 | 1.6668 |
| 0.4397 | 0.0017 | 0.0333 | 2.1499 |
| 0.5319 | 0.0018 | 0.0356 | 2.2788 |
| 0.6395 | 0.0018 | 0.0351 | 2.2607 |
| 0.7301 | 0.0016 | 0.0316 | 1.8323 |
| 0.8315 | 0.0012 | 0.0238 | 1.1871 |
| 0.9313 | 0.0005 | 0.0117 | 0.6445 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| isopropyl benzene + toluene | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1193 | 0.0016 | 0.0119 | 2.1838 |
| 0.2209 | 0.0033 | 0.0226 | 3.5351 |
| 0.3312 | 0.0052 | 0.0311 | 4.5909 |
| 0.4397 | 0.0067 | 0.0360 | 5.2191 |
| 0.5319 | 0.0077 | 0.0373 | 5.3108 |
| 0.6395 | 0.0080 | 0.0351 | 4.8930 |
| 0.7301 | 0.0075 | 0.0302 | 4.0998 |
| 0.8315 | 0.0058 | 0.0210 | 2.9161 |
| 0.9313 | 0.0028 | 0.0080 | 1.3671 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 |

| | | | |
|---|---|---|---|
| isopropyl benzene + meistylene | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1193 | 0.0040 | 0.0078 | 0.3054 |
| 0.2209 | 0.0066 | 0.0133 | 0.4347 |
| 0.3312 | 0.0087 | 0.0177 | 0.4615 |
| 0.4397 | 0.0099 | 0.0202 | 0.5849 |
| 0.5319 | 0.0103 | 0.0209 | 0.6884 |
| 0.6395 | 0.0098 | 0.0199 | 0.6146 |
| 0.7301 | 0.0087 | 0.0173 | 0.5135 |
| 0.8315 | 0.0067 | 0.0126 | 0.4163 |
| 0.9313 | 0.0038 | 0.0058 | 0.3266 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| isopropyl benzene + n-propyl benzene | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1193 | 0.0015 | 0.0015 | 0.3183 |
| 0.2209 | 0.0030 | 0.0032 | 0.5700 |
| 0.3312 | 0.0044 | 0.0045 | 0.8204 |
| 0.4397 | 0.0053 | 0.0053 | 0.9713 |
| 0.5319 | 0.0058 | 0.0056 | 1.1496 |
| 0.6395 | 0.0057 | 0.0054 | 0.8108 |
| 0.7301 | 0.0051 | 0.0049 | 0.5731 |
| 0.8315 | 0.0037 | 0.0038 | 0.4211 |
| 0.9313 | 0.0015 | 0.0017 | 0.3376 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| isopropyl benzene + t-butyl benzene | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0 |
| 0.1193 | 0.0010 | 0.0012 | 0.7048 |
| 0.2209 | 0.0023 | 0.0026 | 1.1378 |
| 0.3312 | 0.0036 | 0.0038 | 1.4736 |
| 0.4397 | 0.0045 | 0.0047 | 1.6979 |
| 0.5319 | 0.0049 | 0.0052 | 1.9101 |
| 0.6395 | 0.0049 | 0.0051 | 1.6254 |
| 0.7301 | 0.0043 | 0.0045 | 1.3577 |
| 0.8315 | 0.0031 | 0.0032 | 1.0356 |
| 0.9313 | 0.0011 | 0.0011 | 0.6028 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| isopropyl benzene + Biphenyl | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1193 | 0.0028 | 0.0125 | 3.6277 |
| 0.2209 | 0.0046 | 0.0245 | 6.0471 |
| 0.3312 | 0.0060 | 0.0349 | 7.8560 |
| 0.4397 | 0.0067 | 0.0419 | 8.8932 |
| 0.5319 | 0.0068 | 0.0448 | 9.0729 |
| 0.6395 | 0.0063 | 0.0440 | 8.2753 |
| 0.7301 | 0.0053 | 0.0394 | 7.0948 |
| 0.8315 | 0.0037 | 0.0295 | 5.0371 |
| 0.9313 | 0.0015 | 0.0142 | 2.4339 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 |

The derived excess parameters adiabatic compressibility ($\beta_{ad}^{E}$), enthalpy ($H^E$) and free volume and ($V_f^E$), at 298.15 K are summarized in Table 4. These excess properties were calculated using the following equations.

The adiabatic compressibility ($\beta_{ad}$) of the medium was calculated from the measured ultrasonic velocity (u) and density (ρ) using the following relation [39–40]:

$$\beta_{ad} = u^{-2}\ \rho^{-1} \quad (4)$$

$$\beta_{ad}^{E} = \beta_{ad} - x_1\,\beta_{ad,1} - x_2\,\beta_{ad,2}, \quad (5)$$

Where $\beta_{ab}$ $\beta_{ab,1}$ and $\beta_{ab,2}$ are the isentropic compressibilities of the mixture, pure component 1 and pure component 2, respectively.

The free volumes ($V_f$) of the mixtures were calculated using their relationship with ultrasonic velocity and viscosity, as described by the following equation:

$$V_f = (M\,U/\,k\,\eta)^{3/2} \ldots (6)$$

.

Where M is the molecular weight (gm)

U is the sound velocity (cm/sec)

η is the viscosity (poise)

k is the constant, equal to $4.28\times10^9$, independence of temperature and $V_f$, the free volume is in milliliters per mole.

The enthalpy (H) of the system can be calculated using the following equation:

$$H = V_m \times P_i \quad \ldots (7)$$

Where $V_m$ is molar volume and $P_i$ is internal pressure.

Excess thermodynamic functions ($Y^E$) provide a direct measure of the deviation of a solution from ideal behaviour. They are defined as the difference between the thermodynamic property of a real mixture and the corresponding property of an ideal solution at the same temperature, pressure, and composition. Excess values for all relevant parameters were calculated using the general formula:

$$Y^E = Y_{exp} - (X_1Y_1 + X_2 Y_2) \quad \ldots(8)$$

Where Y represents the parameter such as intermolecular free length, free volume, internal pressure, adiabatic compressibility and entropy and $X_1$ *and* $X_2$ are the mole fractions of components whose parameters.

The variation of Adiabatic compressibility with mole fraction of isopropyl benzene (cumene) for the binary systems of (A) isopropyl benzene (cumene) + ethyl benzene, isopropyl benzene (cumene) + toluene, isopropyl benzene (cumene) + mesitylene, isopropyl benzene (cumene) + *n*-propyl benzene, isopropyl benzene (cumene) + *tert*-butyl benzene, and isopropyl benzene (cumene) + biphenyl at the 298.15 K is illustrated in Fig. 1. The corresponding values are provided in Tables 3.

The excess value of adiabatic compressibility **($\beta^E_{ab}$)** at the six binary liquid mixtures namely, isopropyl benzene (cumene) + ethyl benzene, isopropyl benzene (cumene) + toluene, isopropyl benzene (cumene) + mesitylene, isopropyl benzene (cumene) + *n*-propyl benzene, isopropyl benzene (cumene) + *tert*-butyl benzene, and isopropyl benzene (cumene) + biphenyl at the 298.15 K are reported in Table 4. The excess adiabatic compressibility **($\beta^E_{ab}$)** values may be explained as a cumulative manifestation of numerous types of intermolecular interactions between the constituent molecules of the mixtures under investigation. The values of excess adiabatic compressibility **($\beta^E_{ab}$)** for the investigated binary mixture of isopropyl benzene (cumene) + ethyl benzene, isopropyl benzene (cumene) + toluene, isopropyl benzene (cumene) + mesitylene, isopropyl benzene (cumene) + *n*-propyl benzene, isopropyl benzene (cumene) + *tert*-butyl benzene, and isopropyl benzene (cumene) + biphenyl as the function of isopropyl benzene (cumene) mole fraction has been reported in Fig. 1. Size and shape difference of molecules have a considerable effect on the sign and magnitude of deviation in isentropic compressibility values. Mutual structure breaking produces positive values of excess adiabatic compressibility **($\beta^E_{ab}$).** The excess adiabatic compressibility **($\beta^E_{ab}$)** can be interpreted in terms of two opposing effects: (i) the loss of mutual dipolar association and differences in the size and shape of unlike molecules, and (ii) dipole–induced dipole and dipole–dipole interactions. The first effect increases the free length of the mixture, as described by Jacobson, leading to a negative deviation in ultrasonic velocity and a positive deviation in adiabatic compressibility. In contrast, the second effect tends to increase molecular cohesion, resulting in a positive deviation in ultrasonic velocity and a negative deviation in adiabatic compressibility. Consequently, the sign and magnitude of **($\beta^E_{ab}$)** reflect the balance between these two competing molecular interactions. The excess adiabatic compressibility **($\beta^E_{ab}$)** data for all binary mixtures of isopropyl benzene (cumene) with aromatic hydrocarbons are graphically presented in Fig. 1 at 298.15 K and atmospheric pressure. The variation of **($\beta^E_{ab}$)** with the mole fraction of isopropyl benzene ($X_1$) shows that all mixtures exhibit positive values. The effect is most pronounced in the cumene–mesitylene system, which displays the highest positive **($\beta^E_{ab}$)** among the studied mixtures. According to Kiyohara and Benson [41], **($\beta^E_{ab}$)** arises from several opposing molecular effects.

The adiabatic compressibility values of six the binary liquid systems rise with mole fraction ($X_1$ ) of isopropyl benzene (cumene), as shown in Table 3 and Fig. 1. The main cause of the shift in ultrasonic velocity is the way that structure affects compressibility. When mixing liquid mixtures, adiabatic compressibility changes, indicating a distinct contraction, Complex creation may be the cause of this variance. The molecular clustering of the other molecules is disrupted by the addition of interacting molecules, which release multiple dipoles for interaction. Thus, the structural arrangement of molecules results in decreasing adiabatic compressibility, thereby showing intermolecular interactions. Similar results in some liquid mixtures are also reported by others and show good agreement with the present results.

The observed positive values may be attributed to the relative sizes of the molecules, which allow increased free volume and reduced dipole–dipole interactions [42]. The trends also suggest a decrease in dipolar interactions with increasing chain length of the aromatic hydrocarbons. Sri Devi *et al*. [43] have noted that positive **($\beta^E_{ab}$)** values can be attributed to the predominance of dispersion forces between unlike molecules. The plots of excess adiabatic compressibility **($\beta^E_{ab}$)**, as displayed in Figure 1, show that for isopropyl benzene (cumene) + ethyl benzene, isopropyl benzene (cumene) + toluene, isopropyl benzene (cumene) + mesitylene, isopropyl benzene (cumene) + *n*-propyl benzene, isopropyl benzene (cumene) + *tert*-butyl benzene, and isopropyl benzene (cumene) + biphenyl exhibit positive deviation over the entire range of mixture composition. The positive excess adiabatic compressibility **($\beta^E_{ab}$)** values are a sign of weak interaction between component molecules, which may be attributed to the mutual disruption in molecules associated with pure liquids. These positive excess adiabatic compressibility **($\beta^E_{ab}$)**, values are accompanied by a decrease in sound velocity over the entire range of composition of isopropyl benzene (cumene). The positive values of excess adiabatic compressibility **($\beta^E_{ab}$)**, may be attributed to the formation of weak bonds by dipole-induced dipole interaction between unlike molecules and the geometrical fitting of component molecules in to each other's structure.

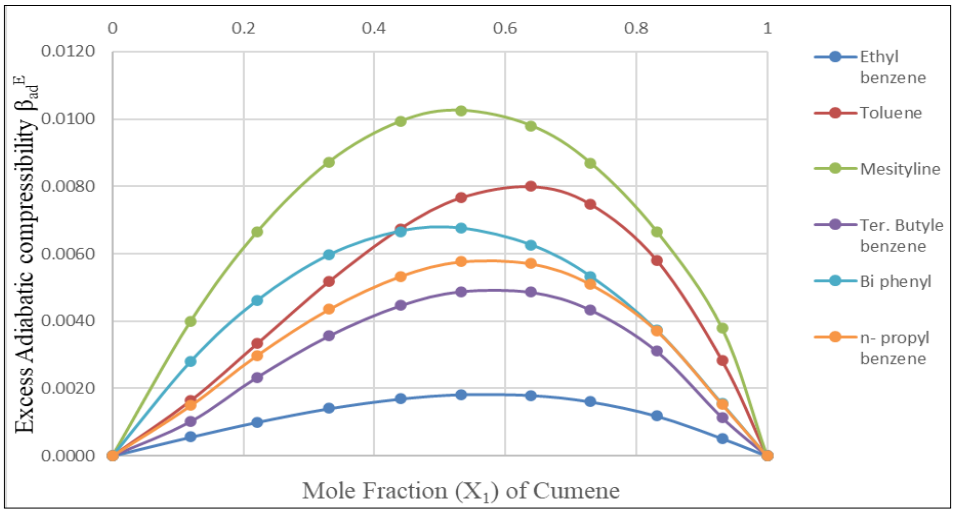



**Fig 1:** Curves of excess adiabatic compressibility ($\beta_{ad}^{E}$) versus the mole fraction of isopropyl benzene (cumene, $X_1$) for the binary mixtures of isopropyl benzene (1) with Aromatic Hydrocarbons (2) at 298.15 K and atmospheric pressure. The solid lines represent values calculated using the Redlich–Kister equation

The experimental results are consistent with this explanation, as most of the studied mixtures exhibit positive excess volumes. This indicates that changes in intermolecular forces dominate over packing effects caused by geometrical constraints, which explains the variation in excess volumes among different hydrocarbons. When comparing maximum excess volumes at equimolar composition, several trends emerge: mixtures with flat or small-substituted hydrocarbons (e.g., ethylbenzene, mesitylene, biphenyl) tend to show negative or slightly positive $V^E$; mixtures with non-flat or moderately substituted hydrocarbons (e.g., t-butylbenzene, isopropylbenzene) exhibit intermediate values; and the highest $V^E$ is observed for cumene + mesitylene, where mesitylene has a flat geometry with three methyl groups in the meta positions around the aromatic ring.

These observations can be interpreted qualitatively in terms of steric and electronic effects. Bulky substituents in the hydrocarbon molecules prevent close approach of the acetate groups, weakening interactions and increasing the excess volume. In contrast, flat molecules with few substituents (toluene, ethylbenzene, mesitylene, biphenyl) allow some residual interactions, resulting in slightly positive, sigmoid, or even negative $V^E$. The steric hindrance imposed by three methyl groups in mesitylene obstructs the approach of the cumene molecules, increasing the occupied volume and thus the excess volume. Similar trends in excess volume with molecular size and substitution have been observed in other non-polar + non-polar mixtures, including cumene with aromatic compounds [44–45]. These results highlight the importance of steric hindrance in controlling dispersive interactions and the progressive masking of non-polar effects of methyl groups during mixing. The free volumes of the pure liquids isopropyl benzene (cumene), ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl—were calculated using the method of Suryanarayana and Kuppusami (Eq. 6). The calculated values are listed in Table 3. Excess free volumes ($V_f^E$)were subsequently determined from the difference between the free volume of the mixture and the ideal free volume (Eq. 8), and these values are also presented in Table 4. The variation of ($V_f^E$) with the mole fraction of isopropyl benzene ($X_1$) at 298.15 K for the six binary mixtures is illustrated in Figure 3. The observed excess free volume can be analyzed in terms of three contributions: physical, chemical, and geometrical. Physical interactions, primarily dispersion forces and other non-specific interactions, generally produce positive contributions to ($V_f^E$). Chemical interactions, including the disruption of hydrogen-bonded structures, also tend to increase excess free volume, whereas specific interactions such as hydrogen bonding or charge-transfer complex formation lead to contraction of the mixture and negative contributions. Geometrical or structural contributions arise from the fitting of one component into the other; differences in molecular size and shape can lead to negative contributions to ($V_f^E$). As shown in Figure 2, ($V_f^E$) is positive across the entire composition range for all six binary mixtures at 298.15 K, indicating predominantly weak intermolecular interactions. For systems where dispersion, induction, and dipolar forces are operative, excess free volume and viscosity generally show positive deviations, while specific interactions leading to complex formation can further enhance these positive deviations.

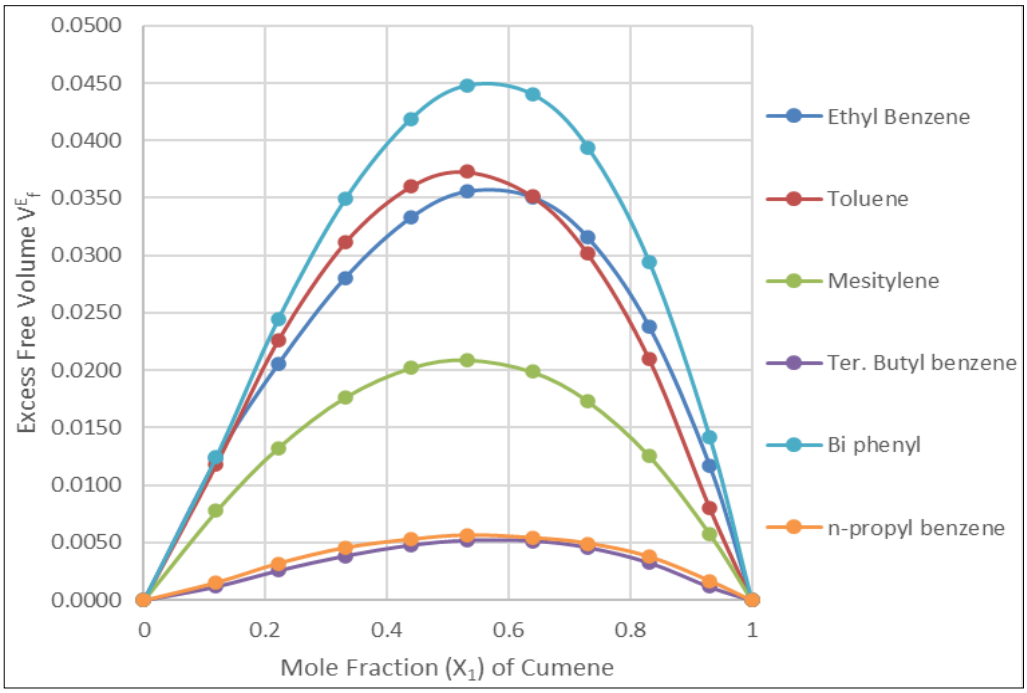



**Fig 2:** Curves of excess refractive indices ($V_f^E$) against the mole fraction of isopropyl benzene (cumene) $x_1$, for the binary mixture (isopropyl benzene (cumene) (1) + Aromatic Hydrocarbons (2)) at 298.15K. The solid lines represent the values calculated from the Redlich−Kister equation.

The excess free volume ($V_f^E$) is positive for all the studied binary mixtures of isopropyl benzene (cumene) with ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl. Positive ($V_f^E$) indicates that the interactions between molecules of the mixed components are weaker than those in the pure components. This behavior is typically observed when one component contains non-polar groups and the other is non-polar or weakly polar. In the present systems, isopropyl benzene is weakly polar, while the aromatic hydrocarbons are nearly non-polar. Upon mixing, the non-polar hydrocarbon molecules intersperse among the isopropyl benzene molecules, reducing interactions among the hydrocarbon molecules and disrupting dispersive interactions between benzene rings. As a result, interactions between unlike molecules are weaker, leading to an overall expansion in volume.

The enthalpy for the pure liquids isopropyl benzene (cumene), Ethyl Benzene, Toluene, mesitylene, *n*-propyl benzene, tert-butyl benzene and biphenyl have been calculated using vide eq. 7. The calculated volumes for all the liquid are enlisted in Table 3. The excess enthalpy ($H^E$) have been calculated through free volume of the mixture and ideal free volume vide eq. 8 the value of excess enthalpy ($H^E$) for these system are also enlisted in Table 4. The variation of excess enthalpy ($H^E$) with mole fraction $(x_1)$ of isopropyl benzene (cumene) at 298.15 K for the binary mixture of isopropyl benzene (cumene) with Ethyl Benzene, Toluene, mesitylene, *n*-propyl benzene, tert-butyl benzene and biphenyl are displayed in Figure 3.

Figure 3 shows the variation of excess enthalpy ($H^E$) with mole fraction of isopropyl benzene (cumene) at the temperature 298.15K For the binary system isopropyl benzene (cumene) with aromatic hydrocarbons (Ethyl Benzene, Toluene, mesitylene, *n*-propyl benzene, *tert*-butyl benzene and biphenyl), the excess enthalpy ($H^E$) values are positive and decreasing with the increase in mole fraction of isopropyl benzene (cumene) up to the mole fraction (0.5) and the increase with increase in mole fraction. Excess enthalpy ($H^E$) is an important parameter for understanding molecular interactions in liquid mixtures. In the present study, for all six binary systems, ($H^E$) decreases as the mole fraction of isopropyl benzene (cumene) increases, as illustrated in Figure 3. According to Nakayama and Shinoda [46], the observed behavior of excess enthalpy ($H^E$) can be interpreted as the result of a balance between positive contributions, arising from hydrogen-bond rupture or dispersive interactions between unlike molecules, and negative contributions, resulting from intermolecular dipolar interactions or geometrical fitting of the molecules. The variation of excess enthalpy ($H^E$) with the mole fraction ($x_1$) of isopropyl benzene (cumene) in binary mixtures with aromatic hydrocarbons (ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl) is shown in Figure 3 at 298.15 K. The excess enthalpy ($H^E$) values are positive for all six binary systems studied. Positive excess enthalpy indicates that the interactions between molecules of the mixed components are weaker than those present in the pure components. This behavior typically occurs when both components are non-polar or weakly polar. In the present systems, isopropyl benzene is weakly polar, while the aromatic hydrocarbons are nearly non-polar. Upon mixing, the non-polar hydrocarbon molecules intersperse among the cumene molecules, reducing the strength of dispersive interactions among the benzene rings. The newly formed interactions between unlike molecules are weaker, resulting in an overall expansion of the mixture [47].

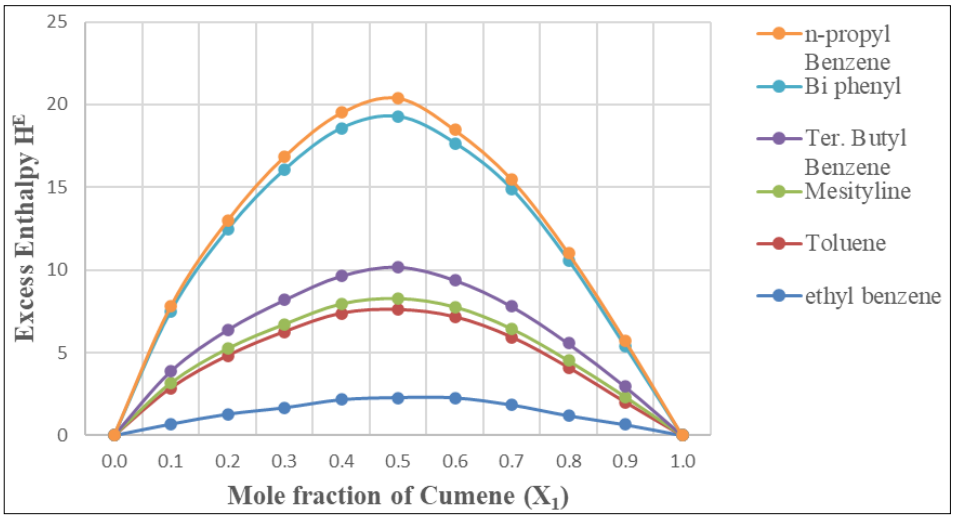



**Fig 3:** Curves of excess enthalpy ($H^E$) against the mole fraction of isopropyl benzene (cumene) $x_1$, for the binary mixture (isopropyl benzene (cumene) (1) + Aromatic Hydrocarbons (2)) at 298.15K. The solid lines represent the values calculated from the Redlich−Kister equation.

## Conclusions

Excess thermodynamic properties represent the difference between the real and ideal mixing behavior of liquid systems. In this study, we report a combined experimental investigation of density, sound velocity, viscosity, and refractive index, along with the derived thermodynamic excess and deviation properties, ($\beta^E_{ad}$, $V_f^E$), and $H^E$) for the pure liquids isopropyl benzene (cumene), ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl and their binary mixtures. These properties are essential for understanding molecular interactions and for designing various chemical and industrial processes. The Redlich–Kister polynomial provided a statistically significant representation of the, ($\beta^E_{ad}$, $V_f^E$, and $H^E$), with an optimal number of coefficients yielding accuracy comparable to or better than the experimental uncertainties. The observed composition dependence of these excess and deviation properties has been successfully interpreted in terms of intermolecular interactions and structural effects in the mixtures.

## Nomenclature

ρ- Density of the mixture (g.cm$^{-3}$)
u -Sound speed of the mixture (m.s$^{-1}$)
$u^E$ -Excess Sound Velocity (m.s$^{-1}$)
$\eta$ –Viscosity (mPa)
M- Molar mass
T-Temperature
P-Pressure
V-Volume
$\eta^E$ -Excess Viscosity(m.Pa)
T- Temperature (Kelvin)
($\beta_{ad}$)- Adiabatic compressibility (Pa$^{-1}$)
(($\beta^E_{ad}$)- Excess adiabatic compressibility(Pa$^{-1}$)
(H)- Enthalpy (J.mol$^{-1}$)
($H^E$)- Excess enthalpy (J.mol$^{-1}$)
($V_f$)- Free volume (M$^3$mol$^{-1}$)
($V_f^E$)-Excess free volume, (M$^3$mol$^{-1}$)
$Y^E$, Thermodynamic excess function
$X_1$ -Mole Fraction of isopropyl benzene (Cumene)

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

## Acknowledgement

The authors thank the Hon'ble Vice-Chancellor Prof. Mukesh Pandey, Bundelkhand University authorities for providing the necessary facilities to carry out the work.

## Funding

The author(s) reported there is no funding associated with the work featured in this article.

## Data availability statement

Data will be made available on request.

## Author Contributions

**Chandra Pal Prajapati:** Data curation, Investigation, Formal Analysis, Software
**Dhirendra Kumar Sharma:** Methodology, Supervision, Writing – original draft

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