

Study of Excess Volumetric and Thermodynamic Properties and Viscosity Modeling for Binary Liquid Mixtures of Isopropyl Benzene (cumene) with Aromatic Hydrocarbons at Temperature 298.15 K and Under Atmospheric Pressure

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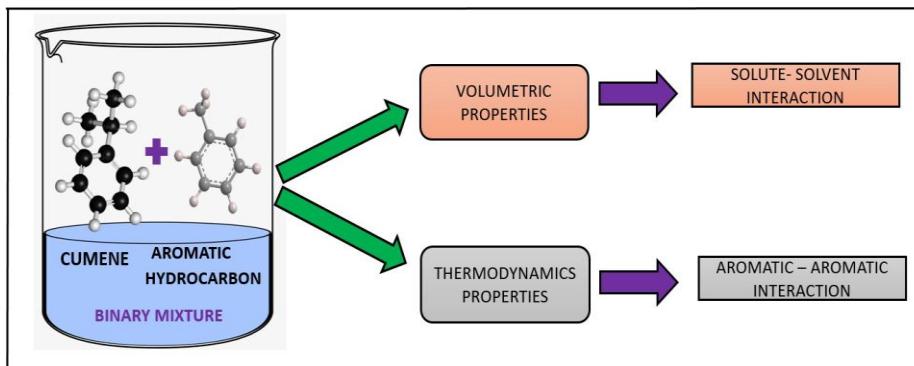
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ABSTRACT

The present discussion embodies the studies on binary mixtures containing 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. For this purpose, the density, viscosity and speed of sound for pure liquids and their binary mixtures were measured within the temperature range 298.15K. Various excess and deviation parameters have been calculated using the measured properties. These properties provide valuable insight into molecular interactions and help predict the behaviour of complex chemical systems. Excess and deviation parameters were fitted to the Redlich–Kister polynomial.

Keywords: Density, viscosity, speed of sound, excess properties, excess free volume, excess internal pressure, Cumene, binary systems, aromatic hydrocarbon.

GRAPHICAL ABSTRACT



INTRODUCTION

Thermodynamic studies of binary solvent systems remain fundamentally important in chemical engineering and industrial chemistry. Rigorous data on properties like density, speed of sound, and viscosity are essential for understanding intermolecular interactions, optimizing process design, and developing efficient separation techniques or solvent formulations [1]. The comprehensive study of binary liquid mixtures offers valuable insights into their behavior, which is essential for both a fundamental scientific understanding and practical engineering applications. In summary, the study of thermodynamic and acoustical properties plays a crucial role in unraveling the physical behavior and molecular interactions in both pure liquids, [2–6] binary liquid mixtures, [7–8] and electrolytic solutions. By examining the excess functions from ideality, researchers can gain insights into the nature and strength of molecular interactions in the binary mixtures. The volumetric and thermodynamic properties are very important for obtaining the fundamental data of various molecular liquids mixtures from different classes of compounds and for understanding the behaviour of interactions occurred between the components of these mixtures. These data are useful in chemical and petrochemical engineering designs with diverse applications: for phase separation processes and waste materials recycling, for surface facilities production operations and pipeline systems, etc., as well as in solutions theory and molecular thermodynamics for confirmation and development of theoretical and empirical models of pure fluids and mixtures.]The strength of the chemical interactions between molecules in a binary mixture is indeed reflected in the fluctuation in the values of the excess parameters. These interactions can manifest through phenomena such as hydrogen bonding, solvation, self association, or other types of molecular recognition as a function of the composition, the molecular sizes, and the shapes of the components and the temperature. A number of studies have been conducted by researchers over the years on mixtures involving 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. Thermophysical and in particular volumetric properties of aqueous mixtures of diols have been measured by various authors since some time ago [9–11]. The thermo physical properties such as the densities, speeds of sound, kinematic and/or dynamic viscosities and the refractive indices, as well as their related magnitudes (the excess/deviation thermodynamic quantities and volumetric/apparent molar quantities) are largely revealed in open literature. In recent years the studies of the thermo physical properties and thermodynamic behavior of *n*-alkane with long chain, both pure and in mixture with different organic compounds, have received a considerable interest. The experimental values of sound velocity (*u*), density (ρ) and viscosity (η) are useful in evaluating thermodynamic properties such as enthalpy (*H*), free volume (V_f), internal pressure (P_i) and several excess parameters which will be very much useful in concerning the nature of intermolecular forces between the component molecules. 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 measurement of internal pressure is essential for understanding the thermodynamic behaviour of liquids. Internal pressure represents the net cohesive force within a liquid, arising from the balance between intermolecular attractive and repulsive forces. This cohesive nature generates an intrinsic pressure that strongly influences the liquid's structural and interactional characteristics. Consequently, internal pressure provides valuable insight into solubility behaviour, as dissolved solutes experience the intrinsic pressure of the surrounding medium. The interactions between solutes and solvent molecules may involve hydrogen bonding, charge-transfer interactions, Coulombic forces, or van der Waals interactions, all of which contribute to the overall cohesiveness and stability of the liquid system.

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), 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 ₉ H ₁₂	80-15-9	CDH, (P) Ltd. New Delhi, India	99.0%	0.1%	Double distillation
Mesitylene	C ₉ H ₁₂	108-67-8	CDH, (P) Ltd. New Delhi, India	99.8%	0.01%	Double distillation
Ethyl benzene	C ₈ H ₁₀	100-41-4	CDH, (P) Ltd. New Delhi, India	99.8%	0.1%	Double distillation
Toluene	C ₇ H ₈	108-88-3	CDH, (P) Ltd. New Delhi, India	99.0%	0.1%	Double distillation
n-Propyl benzene	C ₉ H ₁₂	103-65-1	CDH, (P) Ltd. New Delhi, India	99.0%	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 K₂CO₃, 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 1×10^6 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 ± 1 m.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:

$$U = \lambda \cdot F \quad (1)$$

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.

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

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), ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, 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:

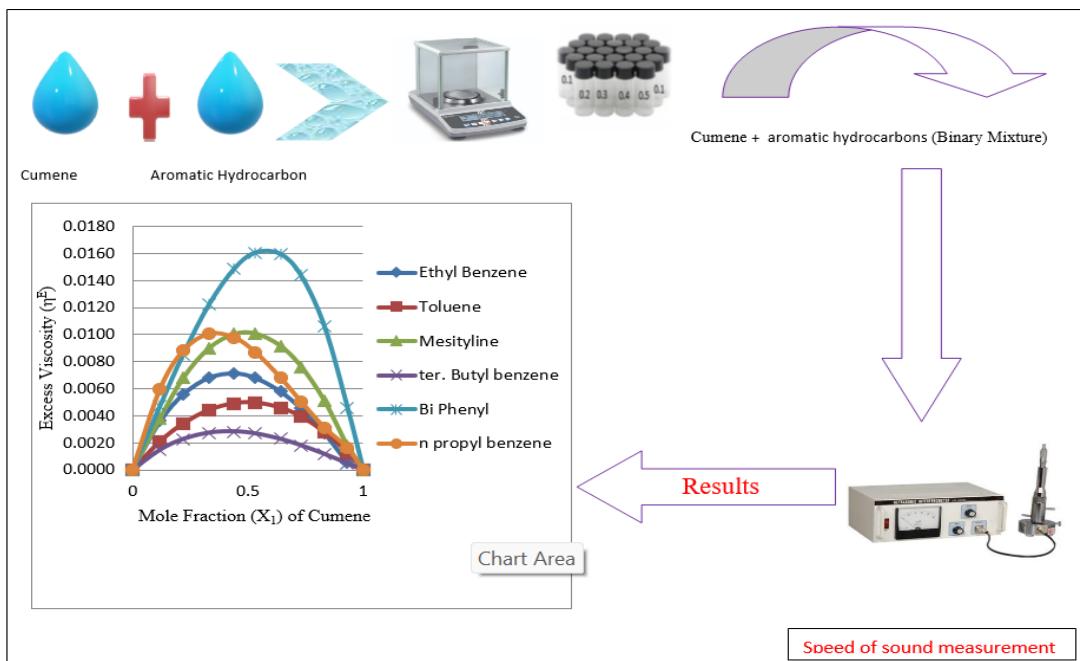
$$Y = x_1 x_2 \sum_{j=1}^p A_{j-1} (x_1 - x_2)^{j-1} \quad (3)$$

Where Y is V_m^E , V_f^E , p_i^E 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 ethylbenzene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl at 298.15 K are summarized in Table 3. Using these measured values, various derived thermodynamic parameters including molar volume (V_m), enthalpy (H), internal pressure (P_i), 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) and Viscosity (η) of Binary Mixtures of Isopropyl Benzene with Aromatic Hydrocarbons at 298.15 K.

Mole fraction Cumene (x_1)	Density (ρ) g.cm ⁻³	Viscosity (η) mPa.s	Speed of Sound (u) ms ⁻¹	Molar volume V_m (cm ³ mol ⁻¹)	Free Volume $V_f \times 10^{-7}$ M ³ mol ⁻¹	Internal pressure $p_i \times 10^5$ N m ⁻²	Enthalpy (H) $\times 10^{-6}$ (J.mol ⁻¹)
isopropyl benzene + ethyl benzene							
0.0000	0.8630	0.6345	1308	123.02	0.3512	2.8014	3.4463
0.1193	0.8612	0.6472	1310	125.16	0.3526	2.7754	3.4737
0.2209	0.8600	0.6633	1314	126.98	0.3537	2.7541	3.4973
0.3312	0.8596	0.6715	1316	128.97	0.3549	2.7294	3.5202
0.4397	0.8592	0.3882	1317	130.94	0.3561	2.7064	3.5438
0.5319	0.8588	0.6931	1318	132.61	0.3571	2.6853	3.5610
0.6395	0.858	0.7042	1320	134.52	0.3582	2.6608	3.5794
0.7301	0.8572	0.7124	1321	136.13	0.3591	2.6378	3.5908
0.8315	0.8564	0.7198	1322	137.90	0.3601	2.6119	3.6018
0.9313	0.8554	0.7249	1324	139.66	0.3611	2.5875	3.6137
1.0000	0.8532	0.7337	1326	140.87	0.3616	2.5691	3.6191
isopropyl benzene + toluene							
0.0000	0.8672	0.5527	1312	106.25	0.3462	3.1354	3.3313

0.1193	0.8628	0.5801	1314	110.26	0.3481	3.0683	3.3875
0.2209	0.8612	0.6046	1315	113.82	0.3498	3.0110	3.4302
0.3312	0.8600	0.6293	1316	117.53	0.3516	2.9488	3.4725
0.4397	0.8592	0.6457	1318	121.23	0.3534	2.8878	3.5100
0.5319	0.8584	0.6706	1390	124.43	0.3548	2.8356	3.5375
0.6395	0.8576	0.6869	1320	128.18	0.3564	2.7745	3.5643
0.7301	0.8568	0.7032	1321	131.44	0.3577	2.7228	3.5824
0.8315	0.8556	0.7191	1322	134.95	0.3592	2.6652	3.5998
0.9313	0.8544	0.7266	1324	138.42	0.3606	2.6085	3.6130
1.0000	0.8532	0.7337	1326	140.87	0.3616	2.5691	3.6191
isopropyl benzene + meistylene							
0.0000	0.8616	0.6449	1338	139.50	0.4753	2.3605	3.2715
0.1193	0.8612	0.6216	1336	139.59	0.4698	2.3875	3.3161
0.2209	0.8608	0.6384	1335	139.66	0.4618	2.4092	3.3527
0.3312	0.8604	0.6551	1334	139.74	0.4546	2.4324	3.3913
0.4397	0.86	0.6718	1333	139.76	0.4486	2.4556	3.4302
0.5319	0.8596	0.6885	1332	139.85	0.4356	2.4756	3.4633
0.6395	0.8592	0.6967	1331	139.89	0.4216	2.4975	3.4999
0.7301	0.8588	0.7048	1330	140.05	0.4085	2.5158	3.5304
0.8315	0.8584	0.7130	1329	140.38	0.3942	2.5364	3.5647
0.9313	0.8576	0.7293	1328	140.54	0.3751	2.5568	3.5985
1.0000	0.8532	0.7337	1326	140.87	0.3616	2.5691	3.6191
isopropyl benzene + n-propyl benzene							
0.0000	0.8624	0.7931	1315	138.61	0.3167	2.7143	3.7622
0.1193	0.8620	0.7896	1316	138.90	0.3236	2.6986	3.7483
0.2209	0.8618	0.7884	1317	139.17	0.3298	2.6846	3.7363
0.3312	0.8614	0.7724	1318	139.45	0.3361	2.6698	3.7230
0.4397	0.8604	0.7664	1319	139.70	0.3417	2.6550	3.7090
0.5319	0.8596	0.7626	1320	139.95	0.3462	2.6421	3.6976
0.6395	0.8588	0.7558	1321	140.10	0.3508	2.6258	3.6788
0.7301	0.8584	0.7524	1322	140.30	0.3544	2.6111	3.6634
0.8315	0.8576	0.74630	1324	140.52	0.3578	2.5956	3.6474
0.9313	0.8560	0.7422	1325	140.74	0.3602	2.5808	3.6323
1.0000	0.8532	0.7337	1326	140.87	0.3616	2.5691	3.6191
isopropyl benzene + t-butyl benzene							
0.0000	0.8624	0.7449	1316	154.77	0.4105	2.3043	3.5665
0.1193	0.8620	0.7445	1317	153.17	0.4055	2.3372	3.5798
0.2209	0.8612	0.7440	1318	151.78	0.4012	2.3648	3.5895
0.3312	0.8604	0.7436	1390	150.27	0.3978	2.3948	3.5986
0.4397	0.8596	0.7420	1320	148.78	0.3946	2.4242	3.6066
0.5319	0.8586	0.7398	1321	147.56	0.3906	2.4488	3.6136
0.6395	0.8572	0.7389	1322	146.01	0.3846	2.4768	3.6164
0.7301	0.8564	0.7373	1323	144.72	0.3788	2.5003	3.6185
0.8315	0.8556	0.7364	1324	143.30	0.3722	2.5266	3.6206
0.9313	0.8548	0.7351	1325	141.90	0.3656	2.5521	3.6215
1.0000	0.8532	0.7337	1326	140.87	0.3616	2.5691	3.6191
isopropyl benzene + Biphenyl							
0.0000	0.7920	0.6108	1118	177.91	0.6809	1.6766	2.9829
0.1193	0.7956	0.6215	1144	173.45	0.6498	1.7844	3.0951
0.2209	0.8036	0.6357	1174	169.70	0.6314	1.8761	3.1839
0.3312	0.8084	0.6510	1186	165.65	0.6124	1.9754	3.2722
0.4397	0.8144	0.6710	1198	161.66	0.5875	2.0732	3.3516
0.5319	0.8248	0.6932	1212	158.31	0.5576	2.1553	3.4120

0.6395	0.8276	0.7308	1242	154.27	0.5202	2.2509	3.4725
0.7301	0.8324	0.7161	1274	150.90	0.4827	2.3315	3.5183
0.8315	0.8436	0.7215	1286	147.14	0.4428	2.4210	3.5623
0.9313	0.8484	0.7295	1300	143.44	0.4006	2.5095	3.5997
1.0000	0.8532	0.7337	1326	140.87	0.3616	2.5691	3.6191

Table 4: Excess thermodynamic parameter V_m^E , V_f^E , p_i^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 molar volume (V_m^E) ($\text{cm}^3\text{mol}^{-1}$)	Excess Free Volume $V_f^E \times 10^{-7}$ $\text{M}^3\text{mol}^{-1}$	Excess Internal pressure $p_i^E \times 10^5/\text{N m}^{-2}$	Excess Enthalpy $H^E \times 10^{-4}(\text{J.mol}^{-1})$
isopropyl benzene + ethyl benzene				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1193	0.0130	0.0123	21.1098	0.6857
0.2209	0.0293	0.0206	39.5149	1.2822
0.3312	0.0487	0.0281	56.1230	1.6668
0.4397	0.0658	0.0333	67.6464	2.1499
0.5319	0.0763	0.0356	72.6363	2.2788
0.6395	0.0804	0.0351	71.6712	2.2607
0.7301	0.0748	0.0316	64.2368	1.8323
0.8315	0.0557	0.0238	47.6727	1.1871
0.9313	0.0211	0.0117	21.7987	0.6445
1.0000	0.0000	0.0000	0.0000	0.0000
isopropyl benzene + toluene				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1193	0.0224	0.0119	4.8505	2.1838
0.2209	0.0396	0.0226	8.2950	3.5351
0.3312	0.0549	0.0311	10.9872	4.5909
0.4397	0.0654	0.0360	12.5109	5.2191
0.5319	0.0695	0.0373	12.8830	5.3108
0.6395	0.0676	0.0351	12.1922	4.8930
0.7301	0.0595	0.0302	10.6290	4.0998
0.8315	0.0424	0.0210	7.7685	2.9161
0.9313	0.0160	0.0080	3.7605	1.3671
1.0000	0.0000	0.0000	0.0000	0.0000
isopropyl benzene + meistylene				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1193	0.0331	0.0078	16.0060	0.3054
0.2209	0.0562	0.0133	25.0779	0.4347
0.3312	0.0752	0.0177	32.3845	0.4615
0.4397	0.0867	0.0202	36.7306	0.5849
0.5319	0.0902	0.0209	38.0133	0.6884
0.6395	0.0863	0.0199	36.4840	0.6146
0.7301	0.0758	0.0173	32.4910	0.5135
0.8315	0.0553	0.0126	24.8903	0.4163
0.9313	0.0257	0.0058	13.9802	0.3266
1.0000	0.0000	0.0000	0.0000	0.0000
isopropyl benzene + n-propyl benzene				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1193	0.0098	0.0015	12.7856	0.3183
0.2209	0.0188	0.0032	21.7225	0.5700

0.3312	0.0265	0.0045	28.9243	0.8204
0.4397	0.0329	0.0053	33.2048	0.9713
0.5319	0.0341	0.0056	34.4569	1.1496
0.6395	0.0315	0.0054	32.9167	0.8108
0.7301	0.0258	0.0049	28.9318	0.5731
0.8315	0.0174	0.0038	21.3551	0.4211
0.9313	0.0095	0.0017	10.4797	0.3376
1.0000	0.0000	0.0000	0.0000	0.0000
isopropyl benzene + t-butyl benzene				
0.0000	0.0000	0.0000	0.0000	0.0
0.1193	0.0472	0.0012	14.1506	0.7048
0.2209	0.0815	0.0026	24.3469	1.1378
0.3312	0.1107	0.0038	32.6084	1.4736
0.4397	0.1298	0.0047	37.5872	1.6979
0.5319	0.1372	0.0052	39.1406	1.9101
0.6395	0.1340	0.0051	37.5850	1.6254
0.7301	0.1204	0.0045	33.2588	1.3577
0.8315	0.0921	0.0032	24.9198	1.0356
0.9313	0.0494	0.0011	12.8774	0.6028
1.0000	0.0000	0.0000	0.0000	0.0000
isopropyl benzene + Biphenyl				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1193	0.0303	0.0125	16.5386	3.6277
0.2209	0.0550	0.0245	28.5802	6.0471
0.3312	0.0754	0.0349	37.8051	7.8560
0.4397	0.0878	0.0419	42.8483	8.8932
0.5319	0.0918	0.0448	43.8987	9.0729
0.6395	0.0879	0.0440	41.2588	8.2753
0.7301	0.0769	0.0394	35.7228	7.0948
0.8315	0.0555	0.0295	25.8405	5.0371
0.9313	0.0242	0.0142	12.2175	2.4339
1.0000	0.0000	0.0000	0.0000	0.0000

The molar volume V_m calculated from the measured values of density (ρ), molar volume (V_m) was calculated using the relation

$$V_m = \frac{(X_1 M_1 + X_2 M_2)}{\rho} \quad (4)$$

Where X_1, X_2 and M_1, M_2 are the mole fraction and molecular weight of the component 1 and 2 respectively.

According to Bingham [39] and Macleod [40] free volume (V_f) can be calculated from the sound velocity and viscosity by the relation given below

$$V_f = (M U / k \eta)^{3/2} \quad (5)$$

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 4.28×10^9 , independence of temperature and V_f , the free volume is in milliliters per mole.

On the basis of dimensional analysis, using free volume concept, the following expression can be used for calculating internal pressure. The internal pressure of a liquid can also be evaluated by using the equation proposed by Suryanarayana [41-42]

$$p_i = bRT \left(\frac{k\eta}{u}\right)^{\frac{1}{2}} \frac{\rho^{2/3}}{M_{eff}^{7/6}} \quad (6)$$

where b is the packing fraction of the liquid which is taken equal to 2 for most of the liquids, k is a constant equal to 4.28×10^9 , M_{eff} ($= x_1M_1 + x_2M_2$) is the effective molecular mass and M is the molar mass of the mixture of pure liquid and T is absolute temperature.

Enthalpy (H) can be calculated by the following equation [43]

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

Where V_m is molar volume and P_i is internal pressure.

The excess thermodynamic function (Y^E) provide a way to represent directly the deviation of a solution from ideal behaviour. The difference between the thermodynamic function of mixing for a real system and the value corresponding to a perfect solution at the same temperature, pressure and composition is called the thermodynamic excess function, denoted by Y^E . Excess values for all the parameters are computed using the general formula

$$Y^E = Y_{exp} - (X_1 Y_1 + X_2 Y_2) \quad (8)$$

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 molar volume (V_m) 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. 4. The calculated volumes for all the liquid are enlisted in Table 3. Determining the excess molar volume (V_m^E) of binary mixes depends on exact measurement of density. For this aim, several experimental approaches are extensively used, each with advantages and constraints [44]. Figures 1 represent variation of excess molar volume (V_m^E) with x_1 (isopropyl benzene (cumene)) at 298.15 yielding a U-shaped nature of the graph is attributed to the equilibria of State effects and steric factors arising from the change of orientation of cumene molecules with change in its mole fraction. For the solutions of cumene with ethyl benzene, toluene, mesitylene, *n*-propyl benzene, *tert*-butyl benzene and biphenyl the graphs are inverted v-shaped. Treszcznowicz et al. [45] and later Aminabhavi et al. [46] observed that excess molar volume (V_m^E) many be discussed in terms of several effects which may be arbitrarily divided into physical, chemical and geometrical contributions. The Physical interact involved mainly

dispersion forces giving a positive contribution. The chemical or specific interactions result in a volume contraction and these include charge-transfer type forces.

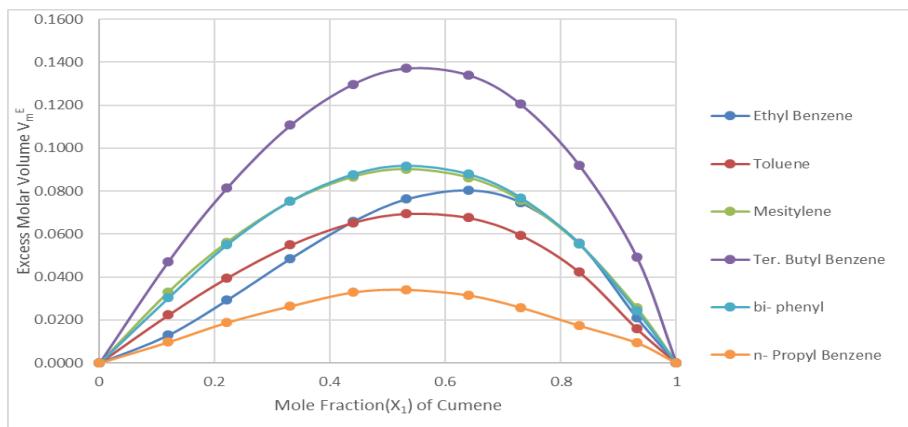


Figure 1: Curves of excess molar volume (V_m^E) against the mole fraction of isopropyl benzene (cumene) x_1 , for the binary mixture (isopropyl benzene (cumene) (1) + Aromatic Hydrocarbons (2) at 298.15K. The solid lines represent the values calculated from the Redlich–Kister equation.

The 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 molar volumes among different hydrocarbons. When comparing maximum excess molar volumes at equimolar composition, several trends emerge: mixtures with flat or small-substituted hydrocarbons (e.g., ethyl benzene, mesitylene, biphenyl) tend to show positive excess molar volume (V_m^E) mixtures with non-flat or moderately substituted hydrocarbons (e.g., t-butylbenzene, isopropylbenzene) exhibit intermediate values; and the highest (V_m^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, ethyl benzene, mesitylene, biphenyl) allow some residual interactions, resulting in (V_m^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 molar 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 [47–48]. 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), ethyl benzene, toluene, mesitylene, n-propyl benzene, tert-butyl benzene, and biphenyl were calculated using the method of Suryanarayana and Kuppusami (Eq. 5). 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 2. 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.

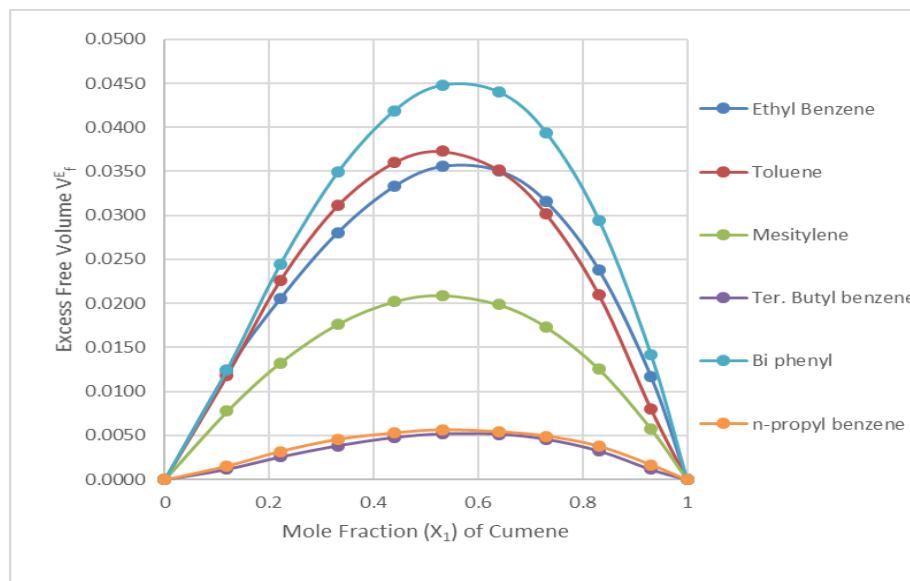


Figure 2: Curves of excess free volume (V_f^E) against the mole fraction of isopropyl benzene (cumene) x_1 , for the binary mixture (isopropyl benzene (cumene) (1) + Aromatic Hydrocarbons (2)) at 298.15K. The solid lines represent the values calculated from the Redlich–Kister equation.

The excess free volume (V_f^E) is positive for all the studied binary mixtures of isopropyl benzene (cumene) with ethyl benzene, toluene, mesitylene, n-propyl benzene, tert-butyl benzene, 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 4.

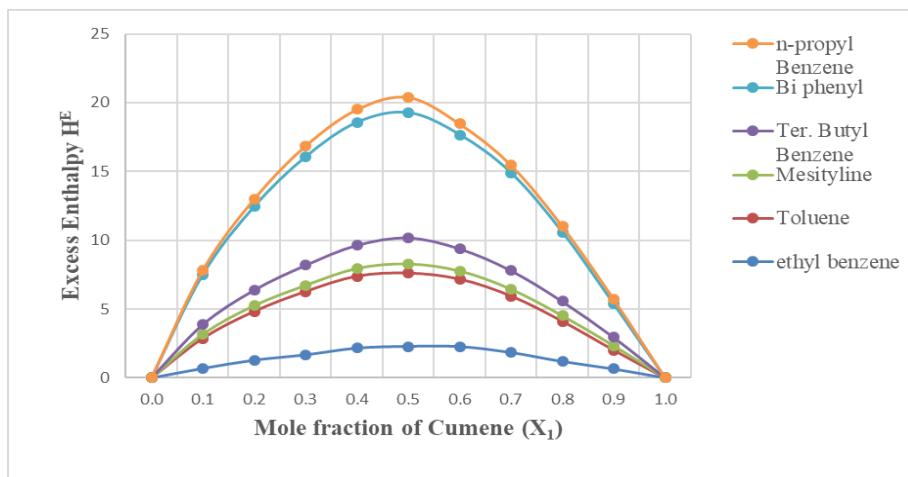


Figure 3: Curves of excess enthalpy (H^E) against the mole fraction of isopropyl benzene (cumene) x_1 , for the binary mixture (isopropyl benzene (cumene) (1) + Aromatic Hydrocarbons (2)) at 298.15K. The solid lines represent the values calculated from the Redlich-Kister equation.

According to Nakayama and Shinoda [49], 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 4 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 [50].

Internal pressure (P_i) is a measure of the cohesive forces in a liquid, resulting from the balance between attractive and repulsive interactions. The attractive forces primarily include hydrogen bonding, dipole-dipole, and dispersion interactions, while repulsive forces, which act at very short intermolecular distances, generally play a minor role under normal conditions. Figure 4 shows the variation of excess internal pressure (p_i^E) with the mole fraction of isopropyl benzene (cumene) at 298.15 K. The internal pressures of the pure liquids cumene, ethylbenzene, toluene, mesitylene, n-propylbenzene, tert-butylbenzene, and biphenyl were calculated using Eq. 6, and the values are listed in Table 3. Excess internal pressures (p_i^E) (were subsequently obtained from the difference between the internal pressure of the mixture and the ideal internal pressure (Eq. 8), and these values are also presented in Table 4. The variation of (p_i^E) with the mole fraction of cumene for all six binary mixtures is displayed in Figure 4. The excess internal pressure is negative across the entire composition range for all mixtures, indicating predominantly weak intermolecular interactions. In each system, the absolute magnitude of (p_i^E) decreases as the concentration of cumene increases. The magnitude of (p_i^E) follows the sequence: ethylbenzene > toluene > mesitylene > n-propylbenzene > tert-butylbenzene > biphenyl. This trend reflects the relative strengths of interactions between cumene and the aromatic hydrocarbons, suggesting that intermolecular interactions are strongest in the cumene + ethylbenzene system and weakest in the cumene + biphenyl system.

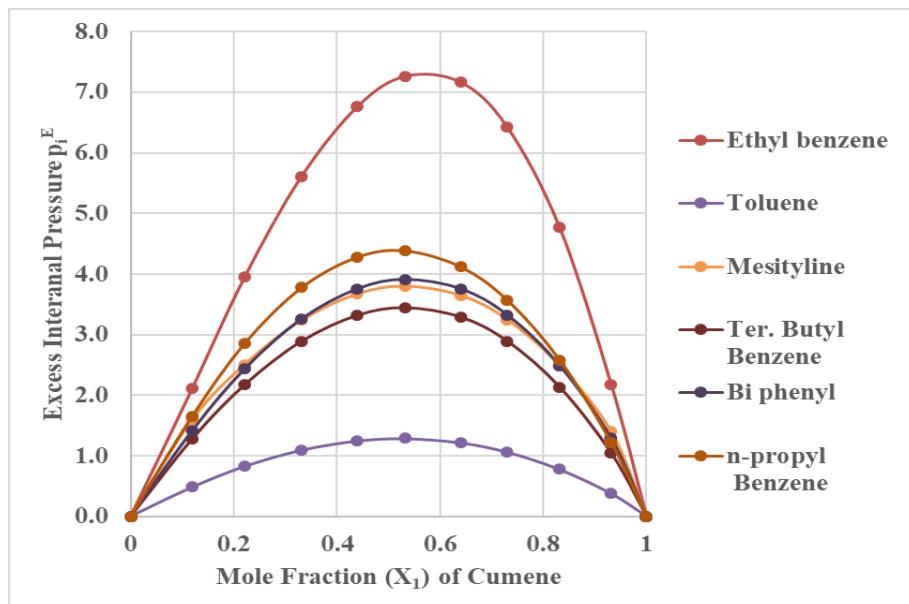


Figure 4: Curves of excess internal pressure (p_i^E) against the mole fraction of isopropyl benzene (cumene) x_1 , for the binary mixture (isopropyl benzene (cumene) (1) + Aromatic Hydrocarbons (2)) at 298.15K. The solid lines represent the values calculated from the Redlich-Kister equation.

The predominant interaction in isopropyl benzene (cumene) + aromatic hydrocarbon mixtures is likely of the electron donor-acceptor (charge-transfer) type [51], involving the π -electrons of the cumene aromatic ring (acting as donor) and the π -electrons of the aromatic hydrocarbon rings (acting as acceptor). Notably, the excess internal pressure (p_i^E) decreases as the number of $-\text{CH}_3$ substituents on the aromatic ring increases, from benzene (no $-\text{CH}_3$) to mesitylene (three $-\text{CH}_3$ groups). This behavior can be attributed to the electron-releasing nature of the methyl groups, which enhances the electron density of the aromatic ring but simultaneously reduces its electron-accepting ability. Consequently, the donor-acceptor interactions between unlike molecules weaken as the number of methyl groups increases, leading to lower (p_i^E) values. Similar trends in (p_i^E) and excess free volume (V_f^E) have been observed in tetrahydrofuran + aromatic hydrocarbon binary mixtures [52]. This interpretation of molecular interactions satisfactorily explains the compositional trends observed in the (p_i^E) values for the present systems.

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, V_m^E , V_f^E , p_i^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 (V_m^E , V_f^E , p_i^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})
- η -Viscosity (mPa)
- M - Molar mass
- T -Temperature
- P -Pressure
- V -Volume
- T - Temperature (Kelvin)
- V_m -molar volume
- (V_m^E)- Excess molar volume
- (H)- Enthalpy (J.mol^{-1})
- (H^E)- Excess enthalpy (J.mol^{-1})
- (V_f)- Free volume ($\text{M}^3\text{mol}^{-1}$)
- (V_f^E)-Excess free volume, ($\text{M}^3\text{mol}^{-1}$)
- (P_i)- Internal pressure (N m^{-2})

- (p_i^E) - Excess internal pressure ($N\ m^{-2}$)
- 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.

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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

Suneel Kumar: Software, Validation, methodology

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