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Data Article

Thermodynamic and spectroscopic studies of intermolecular interactions between isoamyl alcohol and monocyclic aromatic non-ideal binary liquid mixtures



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ABSTRACT

The thermodynamic properties such as excess volume (V^E) , excess Gibbs free energy (G^{*E}) , deviation in viscosity $(\Delta \eta)$ and deviation in isentropic compressibility $(\Delta \kappa_s)$ have been calculated using the experimental data of density (ρ) , viscosity (η) and speeds of sound (u) values of binary mixtures namely; isoamyl alcohol (IAA) + chlorobenzene (CB), + benzonitrile (BN), + aniline (AL), + benzaldehyde (BZ) and + nitrobenzene (NB) over the entire range of mole fraction at temperature 298.15, 303.15 and 308.15 K and under atmospheric pressure. The obtained results were fitted to the Redlich-Kister (R-K) equation to determine the adjacent binary coefficients with errors. The calculated parameters were discussed in terms of intermolecular interactions such as H-bonding, $OH-\pi$, and molecules fitting interactions in the non-ideal solutions. Further, the pure liquids and their mixture concentrations were characterized by FT-IR, and 1H -NMR spectral technologies and using these spectral results elucidate intermolecular interaction (H-bond) in dissimilar molecules.

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Specifications table

Subject area Physical chemistry and chemical thermodynamics

Compounds Isoamyl alcohol, chlorobenzene, benzonitrile, aniline, benzaldehyde and nitrobenzene

Data category Physicochemical properties, density, viscosity, and speed of sound

Data acquisition format FT-IR and ¹H-NMR spectral analysis

Data type Calculated and analysis

Procedure Measurement of density, viscosity, and speed of sound of above-mentioned compounds, estimate intermolecular

interactions in unlike molecules by using volumetric, viscometric and acoustic properties

Data accessibility Data is provided with this article

I. Rationale

The thermodynamic properties of pure components and multicomponent mixtures are utilized to investigate the intermolecular interactions between the different components of the mixtures and understand engineering applications concern-

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Table 1Sample description of the chemicals used.

Compound	CAS Registry NO.	Source	Mass fraction purity	Analysis method	Purification method
Isoamyl alcohol (C5H12O)	123-51-3	Alfa aesar	≥ 99.0%	GC	-
Chlorobenzene (C ₆ H ₅ Cl)	108-90-7	Alfa aesar	≥ 99.9%	GC	-
Benzonitrile (C_6H_5CN)	100-47-0	Alfa aesar	≥ 99.0%	GC	-
Aniline $(C_6H_5NH_2)$	62-53-3	Alfa aesar	≥ 99.0%	GC	-
Benzaldehyde (C_6H_5CHO)	100-52-7	Alfa aesar	≥ 99.0%	GC	-
Nitrobenzene (C ₆ H ₅ NO ₂)	98-95-3	Alfa aesar	$\geq 99.0\%$	GC	-

ing mass transfer, heat transfer and fluid flow [1]. The thermophysical properties of multicomponent mixtures are very high importance and primarily essential in all aspects for the scientific community, which can be a fruitful source of information regarding the macroscopic effects of the various types of intermolecular forces which are present in liquid mixtures [2,3]. The information on thermophysical properties is again essential in aiding with the basic understanding of physical and chemical behavior, including their macroscopic and microscopic characteristics. The physiochemical properties of multicomponent systems are of significance to support in assimilation of the structure and property of the mixtures and its correlations, which will enhance a predictive modeling [4].

Volumetric properties of multicomponent liquid mixtures are complex properties due to they depend not only on shape, size and chemical nature of the components of a mixture, but also on the solute + solute, solvent + solvent, solute + solvent interactions, and structural effects arising from interstitial accommodation due to differences in molar volume and free volume between solution components. The viscometric properties are needed in all the situations involving liquid flow and thickness of solution, such as in irrigation, power generation and in most chemical industries. Consequently, viscosity and its deviations are of vital importance for industrial and academic communities. Besides, it is very useful in solution chemistry to understanding the molecular interactions between dissimilar molecules in the multicomponent mixture. The acoustic properties have been extensively used to study physicochemical behavior and intermolecular interactions in unlike molecules of a variety of multicomponent liquid mixtures. These properties studies have proven to be a very useful tool in elucidating the structural interactions among the components which are of great importance in helping to understand the nature and extent of the patterns of molecular aggregation that exist in liquid mixtures [5].

Isoamyl alcohol (IAA) is an ingredient of Kovac's reagent, used for the bacterial diagnostic indole test. It is mainly used as a solvent for surfaces and laquer baths, inks for print, and dyes for wool as well as in the chemical production of photographic and pharmaceutical substances [6]. Chlorobenzene (CB) is widely used in the manufacture of certain pesticides like DDT and working an intermediate in the making of herbicides, rubber, and dyestuff [7]. Benzonitrile (BN) is widely used in pharmaceutical chemistry and also working a precursor to the resin benzoguanamine. Aniline (AL) is used in the preparation of synthetic dyes, drugs and as an accelerator in the vulcanization of rubber [8]. Benzoin formed from benzaldehyde (BZ) and it is used as "tincture benzoin" in medicine for throat infection. Generally, it is a very important component in process manufacturing of the flavor, fragrance, pharmaceuticals, dye industries and can be used precursor to certain acridine dyes as well [9]. Nitrobenzene (NB) is used as a precursor to rubber chemicals, dyes, pesticides, explosives, and pharmaceuticals. Further, it is also used in shoe and floor polishes, leather dressings [10].

The aim of present work, the study of unlike binary mixtures {liquid + liquid} containing reporting new experimental data of ρ , u and η for binary systems of {IAA (1) + CB (2)}, {IAA (1) + BN (2)}, {IAA (1) + AL (2)}, {IAA (1) + BZ (2)} and {IAA (1) + NB (2)} as a function of composition at T = (298.15 to 308.15) K with the step of 5 K and under atmospheric pressure. From these experimental results, excess parameters such as excess volumes (V^E) and excess Gibbs free energy (G^{*E}) and deviation functions such as viscosity deviation ($\Delta \eta$) and deviation in isentropic compressibility ($\Delta \kappa_s$) were computed at studied temperatures. These parameters fitted by the Redlich–Kister (R-K) polynomial equation. The obtained results were discussed in terms of H-bond, OH- π , and molecules fitting inter-molecular interactions between similar and dissimilar molecules. Further, the investigation of temperature effect on thermodynamic properties and their derived parameters. Also, FT-IR and ¹H-NMR spectral technologies were used to determine the possible H-bonding interaction. From the literature survey, the thermodynamic functions of the binary mixture of isoamyl alcohol with selected benzene mono substituted components (BMSC) have not still reported.

2. Procedure

2.1. Materials

All studied chemicals were manufactured by the Alfa Asar company. Table 1 shows the CAS registry number, analysis method, and purities of these substances provided by the supplier. No further purifications of chemicals were performed. The quality of these used chemicals was verified with a gas chromatograph (GC) equipped with a flame ionization detector (FID). The GC did not show significant impurities, and therefore, the resulting purity values for all the substances coincided with those indicated by the manufacturer. Also, the experimental values of the densities, viscosities and sound velocities of

Table 2 Comparison of experimental values of density (ρ) , viscosity (η) and speed of sound (u) with available corresponding literature values of components at temperatures $T=(298.15,\ 303.15\ \text{and}\ 308.15)\ \text{K}$.

component	T/K	10^{-3}	$\rho/(\mathrm{kg.}\ \mathrm{m}^{-3})$	10 ³ . $\eta/($	kg. m^{-1} . s^{-1})	u/	$u/(m. s^{-1})$	
		Exptl.	Lit.	Exptl.	Exptl.	Lit.	Exptl.	
IAA	298.15	0.8070	0.80712 [73]	3.7400	3.740 [73]	1234.9	1234.9 [74]	
	303.15	0.8030	0.8031 [5]	3.2620	3.2622 [5]	1197.3	1197.4 [5]	
	308.15	0.7969	0.7971 [74]	2.6545	2.6548 [74]	1151.0	-	
CB	298.15	1.1001	1.100858 [75]	0.7549	0.755 [75]	1269.1	1269 [75]	
	303.15	1.0955	1.095459 [75]	0.7257	0.7258 [76]	1250.0	1250.0 [77]	
	308.15	1.0896	1.089705 [75]	0.6789	0.679 [75]	1239.8	1232.0 [77]	
BN	298.15	1.0008	1.0009 [78]	1.2369	1.237 [78]	1592.4	1592.6 [79]	
	303.15	0.9963	0.9964 [78]	1.1101	1.111 [78]	1582.2	1582.4 [79]	
	308.15	0.9918	0.9919 [78]	1.0628	1.063 [78]	1570.6	1570.7 [79]	
AL	298.15	1.0174	1.017511 [80]	3.6900	3.690 [78]	1637.8	1637.8 [80]	
	303.15	1.0131	1.013232 [80]	3.1910	3.190 [78]	1619.3	1619.3 [80]	
	308.15	1.0085	1.0086 [78]	2.8010	2.800 [78]	1595.3	1595.1 [81]	
BZ	298.15	1.0442	1.04437 [82]	1.3921	1.3923 [83]	1460.3	1460.5 [82]	
	303.15	1.0386	1.0357 [10]	1.3201	1.3202 [10]	1452.2	1452.0 [10]	
	308.15	1.0312	1.0313 [84]	1.2484	1.2486 [84]	1442.1	1442.0 [84]	
NB	298.15	1.1971	1.1972 [85]	1.8093	1.8095 [85]	1461.0	1461.0 [31]	
	303.15	1.1913	1.1915 [85]	1.6592	1.6595 [85]	1413.2	1441.0 [84]	
	308.15	1.1862	1.1864 [85]	1.5285	1.5286 [85]	1423.1	1423.0 [31]	

the pure chemicals are compared with available published data at different temperatures are listed in Table 2. In all cases, our experimental results agree with the literature values.

2.2. Characterization

¹H-NMR spectra of pure components and their mixture were determined by Bruker Advance HD 400 MHz NMR instrument (Bruker Co.), in which deuterium reagent CDCl₃ was used. The frequency of nuclear magnetic resonance changes was more noticeable and effectively displayed the chemical structure of compounds. The chemical shifts of the peaks of interest were determined using peak pick facility (Mestrenova software).

The Fourier transform infrared (FT-IR) spectra of pure components and their equimolar mixture were recorded by using a resolving power of 1 cm $^{-1}$ and the variation range of (4000 to 400) cm $^{-1}$ of a Nicolet (Nexus 670) FTIR spectrometer. This spectrometer has an automatic alignment of energy optimization and a dynamic alignment and was fitted two convergent BaF $_2$ particles to measure the sample solution. The spectrometer was calibrated in normal temperature and pressure. And then, it is measured in the FT-IR spectrometer with a 10 μ L sample solution, and the sample thickness was less than 2 μ m. All FT-IR spectral experiments of each sample were performed at room temperature and atmospheric pressure. The deconvolution of the peaks was performed in Microsoft Excel and Origin 8.0 software.

2.3. Equipments and procedure

2.3.1. Measurements of mass and mole fraction

All the examination of pure solvent, co-solvents, and their mixed binary samples were prepared freshly and retained at the required temperature for 24 h to ensure their solubility at the temperature. These prepared solutions were kept in air-tight Stoppard glass vial and closed firmly with parafilm until further use. For the measurement of the mass of each sample, an electronic single pan mass analytical balance (Dhona100 DS model) was used with a precision of $\pm 1 \times 10^{-8}$ kg. The required parameters are measured on the same day, and immediately after preparing each one sample.

2.3.2. Measurement of density

The density of solvent/co-solvents or binary {solvent + co-solvent} molecule mixtures was measured using a pycnometer of 25 cm³ [11]. The pycnometer was calibrated with doubly distilled deionized and degassed water at three equidistant temperatures of (298.15 to 308.15) K with a temperature in space of 5 K under atmospheric pressure. The pycnometer was filled with an investigation sample by using a syringe [12] and kept for a minimum of 30 minutes into a thermostatic water bath with an agitator and thermostatically controlled water bath. To carry out this experimental procedure repeated three times and as the outcome of density for a designated requirement.

The density (ρ) equation was mentioned as Eq. 1:

$$\rho = \frac{m}{V} \tag{1}$$

where m was determined by the electronic analytical balance and V was molar volume. The experimental values of density for binary mixtures of IAA + CB, + BN, + AL, + BZ and + NB are given in Tables 3 and 5 at temperature 298.15, 303.15 and 308.15 K.

Table 3 Values of density (ρ) and excess volume $(V^{\rm E})$ for all the studied binaries at different temperatures.

	T = 2	298.15 K	T = 3	303.15 K	T = 3	308.15 K
	10^{-3} . ρ /	10 ⁶ .V ^E /	10^{-3} . $\rho/$	10 ⁶ .V ^E /	10^{-3} . $\rho/$	10 ⁶ .V ^E /
XIAA	$(kg. m^{-3})$	$(m^3. mol^{-1})$	$(kg. m^{-3})$	$(m^3. mol^{-1})$	$(kg. m^{-3})$	$(m^3. mol^{-1})$
		Isoamyl alc	ohol (1) + Cl	nlorobenzene (2)	
0.0000	1.1001	0.000	1.0955	0.000	1.0896	0.000
0.0933	1.0791	-0.700	1.0724	-0.567	1.0654	-0.460
0.1853	1.0567	-1.296	1.0510	-1.255	1.0431	-1.072
0.2823	1.0342	-2.036	1.0280	-1.939	1.0190	-1.653
0.3778	1.0091	-2.475	1.0027	-2.341	0.9930	-1.986
0.4934	0.9798	-3.099	0.9713	-2.724	0.9605	-2.246
0.5832	0.9539	-3.236	0.9450	-2.792	0.9341	-2.286
0.6822	0.9231	-3.102	0.9137	-2.564	0.9032	-2.080
0.7849	0.8880	-2.542	0.8798	-2.093	0.8688	-1.512
0.8917	0.8481	-1.409	0.8411	-1.056	0.8331	-0.815
1.0000	0.8070	0.000	0.8030	0.000	0.7969	0.000
		Isoamyl al	lcohol(1) + I	Benzonitrile (2)		
0.0000	1.0008	0.000	0.9963	0.000	0.9918	0.000
0.0938	0.9917	-1.042	0.9867	-0.999	0.9812	-0.925
0.1863	0.9819	-2.001	0.9737	-1.621	0.9677	-1.515
0.2836	0.9706	-2.916	0.9606	-2.344	0.9526	-2.050
0.3794	0.9560	-3.454	0.9450	-2.764	0.9370	-2.487
0.4953	0.9354	-3.781	0.9248	-3.118	0.9150	-2.651
0.5848	0.9169	-3.738	0.9067	-3.087	0.8970	-2.640
0.6837	0.8950	-3.476	0.8856	-2.898	0.8746	-2.293
0.7861	0.8699	-2.877	0.8600	-2.200	0.8508	-1.801
0.8924	0.8409	-1.809	0.8332	-1.357	0.8249	-1.062
1.0000	0.8070	0.000	0.8030	0.000	0.7969	0.000
		Isoamyl	alcohol (1) -	+ Aniline (2)		
0.0000	1.0174	0.000	1.0131	0.000	1.0085	0.000
0.0843	1.0104	-1.263	1.0034	-1.022	0.9950	-0.699
0.1691	1.0002	-2.247	0.9941	-2.097	0.9790	-1.153
0.2604	0.9870	-3.092	0.9802	-2.869	0.9642	-1.841
0.3521	0.9715	-3.700	0.9625	-3.263	0.9491	-2.484
0.4657	0.9493	-4.106	0.9401	-3.629	0.9271	-2.886
0.5560	0.9290	-4.101	0.9204	-3.666	0.9088	-3.058
0.6577	0.9056	-3.942	0.8966	-3.436	0.8861	-2.933
0.7656	0.8780	-3.344	0.8691	-2.807	0.8603	-2.489
0.8805	0.8447	-2.044	0.8378	-1.705	0.8281	-1.240
1.0000	0.8070	0.000	0.8030	0.000	0.7969	0.000
				enzaldehyde (2)		
0.0000	1.0442	0.000	1.0386	0.000	1.0312	0.000
0.0930	1.0386	-1.752	1.0270	-1.438	1.0191	-1.123
0.1848	1.0274	-2.960	1.0127	-2.301	1.0020	-1.723
0.2816	1.0118	-3.874	1.0002	-3.475	0.9866	-2.633
0.3771	0.9941	-4.542	0.9821	-4.055	0.9671	-3.070
0.4926	0.9680	-4.876	0.9554	-4.254	0.9424	-3.474
0.5824	0.9454	-4.864	0.9340	-4.301	0.9214	-3.564
0.6816	0.9171	-4.433	0.9066	-3.894	0.8966	-3.442
0.7844	0.8860	-3.711	0.8751 0.8401	-3.027	0.8671	-2.801
0.8914	0.8491	-2.274		-1.715	0.8307	-1.289
1.0000	0.8070	0.000	0.8030	0.000 (itrobanzana (2)	0.7969	0.000
0.0000	1.1971	0.000	1.1913	itrobenzene (2) 0.000	1.1862	0.000
0.0000	1.1812	-1.984	1.1702	-1.527	1.1602	-1.112
0.0937	1.1570	-3.240	1.1702	-2.800	1.1350	-2.303
0.1801	1.1370	-4.534	1.1403	-3.900	1.1037	-3.135
0.2834	1.1008	-5.458	1.0865	-4.656	1.0700	-3.681
0.3791	1.0593	-6.104	1.0456	-5.316	1.0267	-4.087
0.5845	1.0234	-6.242	1.0094	-5.373	0.9900	-4.044
0.6834	0.9780	-5.744	0.9658	-4.990	0.9472	-3.676
0.7859	0.9287	-4.870	0.9038	-4.101	0.9007	-2.946
0.7833	0.8719	-3.109	0.8612	-2.336	0.8512	-1.867
1.0000	0.8070	0.000	0.8030	0.000	0.7969	0.000

The standard uncertainty components u for each variable are u(T)= ± 0.01 K, u(x) = $\pm 1 \times 10^{-4}$, u(p) = ± 1.0 kPa. u(ρ) = $\pm 2 \times 10^{-2}$ g.cm⁻³ and the combined expanded Uncertainty is $U(V^E \times 10^6)$ = $\pm 2 \times 10^{-2}$ m³. mol⁻¹ at 0.95 level of confidence, respectively.

2.3.3. Measurement of viscosity

The viscosity of pure components and their binary liquid systems was calculated by using a suspended levelUbbelohde-type viscometer [13] with 0.8 - 0.9 mm diameter capillary measured. The viscometer was calibrated by using the triple-distilled water range of temperature from 298.15 K to 308.15 K and using a timer with a time control accuracy of ± 0.01 s. The viscosity of the solutions (η) were obtained by the following equation [14]:

$$=\rho\left(At-\frac{B}{t}\right)\tag{2}$$

here, ρ is the density, t is the solution flow time, and A and B are the viscometer constants. The viscometer was filled with every one of the measured samples and placed in a thermostatic water bath with temperature-controlled for a minimum of 30 min, the deviation of the examined values was within ± 0.03 s. Then, the flow time of the identical or non-identical binary mixtures was measured by using a digital stopwatch with an error ± 0.01 s. Every binary mixture needed to be measured more than 5 times. The final viscosity obtained from the average value of 5 measurements. The obtained data of viscosity from Eq. 2 for binary mixture of IAA - CB, IAA -BN, IAA - AL, IAA - BZ, and IAA - NB are given in Table 4 at T = (298.15, 303.15 and 308.15) K.

2.3.4. Measurement of speed of sound

The speed of sound values of pure IAA, pure co-solvents and their binary liquid mixtures were measured at studied temperatures (298.15 K to 308.15 K) under atmosphere pressure using ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz [15].

The interferometer cell was filled with the test liquid, and the required temperature of the solution was maintained constant within ∓ 0.01 K by circulation of water from a thermostatically regulated water bath through the water-jacketed cell. When the liquid attained the temperature of the bath, the micrometer screw was slowly moved till the anode current meter showed a maximum and the reading of the micrometer was noted. This distance between the quartz transducer and the reflector plate was displaced by moving the screw downwards. To best accuracy of the measurement, numerous maxima were allowed to pass and their number \mathbf{n} (in present case 25) was counted. All maxima were recorded with the highest swing of a needle on the micrometer scale. Using the following relations velocity of sound in liquid medium can be measured.

$$u = df (3)$$

$$d = n_{\overline{2}} \tag{4}$$

where d is the separation between successive adjacent maximum anode current and f is the frequency of the wave (2 MHz). If wave increase or decrease the distance and the variation is exactly one half of the wavelength ($\lambda/2$) or its multiple, the anode current again becomes maximum. Among the 25 readings, with permutations and combinations of the first three and last three readings, nine velocities were calculated for each run. The average of nine velocity values gives the velocity of the sound of a particular test sample. The calculated speed of sound values for that mixture of each co-solvent with IAA are shown in Table 5 at temperature 298.15 K, 303.15 K and 308.15 K. The estimated uncertainties of measured density, viscosity and speed of sound were, $\pm 2 \times 10^{-2}$ g, cm⁻³, $\pm 28 \times 10^{-3}$ m²/s and $\pm 0.5\%$.

A thermostatic water bath was used to maintain required temperature stability within ± 0.01 K (INSREF model; IRI-016C, India) [16].

3. Data, value, validation

3.1. Excess volume

The V^E was calculated from using experimental ρ values of like or unlike binary systems, and according to Eq. 5 [17];

$$V^{E} = \frac{\sum_{i=1}^{2} (x_{i} M_{i})}{\rho_{m}} - \sum_{i=1}^{2} \frac{x_{i} M_{i}}{\rho_{i}}$$
 (5)

where, ρ_m = density of {solvent+ co-solvent) mixtures,

 ρ_i = density of pure components,

 x_i = mole fraction of pure compounds,

 M_i = relative molar mass of pure components, respectively.

The obtained excess volume data for the non-ideal binaries of (IAA with BMSC) at temperatures T = (298.15 to 308.15) K were tabulated in Table 3.

The binary mixture of V^E values deviation from ideality will take place in three categories, such as (1) positive V^E ; indicated that the total volume of the binary system increased compared with individual component volume, (2) negative V^E ; designated that the total volume of the binary mixture decreased compared with individual component volume, and (3) zero V^E ; unchanged volume, it is observed in case of binary system of no interactions in molecules. The positive V^E phenomenon was due to the following factors: (i) disruption of self-associated molecules through hydrogen bonding or

Table 4 Values of viscosity (η) , deviation in viscosity $(\Delta \eta)$ and excess Gibbs free energy of activation of viscous flow (G^{*E}) for all the studied binaries at various temperatures.

		98.15 K		T = 30	03.15 K			08.15 K	
ΧIAA	10^3 . $\eta/$ (kg. m ⁻¹ . s ⁻¹)	10 ³ . $\Delta \eta$ / (kg. m ⁻¹ . s ⁻¹)	10 ³ . <i>G</i> * ^{<i>E</i>} /(N. mol ⁻¹)	10 ³ . η / (kg. m ⁻¹ . s ⁻¹)	10 ³ . $\Delta \eta$ / (kg. m ⁻¹ . s ⁻¹)	10 ³ . <i>G</i> * ^E / (N. mol ⁻¹)	10^3 . $\eta/$ (kg. m ⁻¹ . s ⁻¹)	10 ³ . $\Delta \eta$ / (kg. m ⁻¹ . s ⁻¹)	10 ³ . <i>G</i> * ^{<i>E</i>} /(N. mol ⁻¹
				Isoamyl alco	ohol (1) + Chloro	obenzene (2)			
0.0000	0.755	0.000	0.00	0.726	0.000	0.00	0.679	0.000	0.00
0.0933	1.183	0.150	179.5	1.100	0.138	165.7	1.000	0.137	156.6
0.1853	1.591	0.283	267.4	1.434	0.239	239.5	1.255	0.210	215.3
0.2823	1.977	0.380	302.4	1.767	0.326	285.3	1.550	0.314	268.3
0.3778	2.323	0.440	303.8	2.096	0.412	288.2	1.807	0.382	278.6
0.4934	2.712	0.484	281.6	2.410	0.433	265.3	2.062	0.408	255.5
0.5832	2.973	0.477	249.3	2.639	0.435	238.0	2.253	0.422	234.7
	3.213	0.477	200.6	2.849	0.393	194.0	2.376	0.349	194.0
0.6822 0.7849		0.343		2.989	0.393	132.7	2.491		
0.7849	3.441 3.712	0.343	148.0 93.81	3.141	0.273	70.62	2.530	0.261 0.090	132.2 56.52
		0.000				0.00			
1.0000	3.740	0.000	0.00	3.262	0.000		2.655	0.000	0.00
0 0000	1 227	0.000	0.00		cohol (1) + Benz		1.002	0.000	0.00
0.0000	1.237	0.000	0.00	1.110	0.000	0.00	1.063	0.000	0.00
0.0938	1.659	0.187	95.10	1.458	0.146	91.71	1.319	0.107	74.22
0.1863	2.028	0.323	155.2	1.768	0.257	152.4	1.584	0.225	131.2
0.2836	2.371	0.421	189.2	2.102	0.382	189.8	1.830	0.316	162.0
0.3794	2.690	0.500	198.6	2.370	0.443	197.8	2.031	0.364	169.6
0.4953	3.012	0.530	190.4	2.643	0.467	186.1	2.245	0.394	165.2
0.5848	3.229	0.523	169.8	2.838	0.470	171.0	2.378	0.385	150.5
0.6837	3.426	0.471	140.7	2.997	0.416	140.3	2.486	0.335	124.2
0.7861	3.607	0.395	106.5	3.140	0.338	105.3	2.574	0.260	91.01
0.8924	3.701	0.221	56.30	3.243	0.213	52.85	2.621	0.138	46.61
1.0000	3.750	0.000	0.00	3.262	0.000	0.00	2.655	0.000	0.00
					alcohol (1) + Ar				
0.0000	3.690	0.000	0.00	3.191	0.000	0.00	2.801	0.000	0.00
0.0843	3.690	-0.004	-8.270	3.193	-0.005	-6.635	2.779	-0.010	-5.631
0.1691	3.690	-0.008	-14.69	3.194	-0.009	-13.84	2.760	-0.017	-9.584
0.2604	3.691	-0.013	-20.19	3.195	-0.015	-19.27	2.740	-0.023	-14.59
0.3521	3.691	-0.017	-24.22	3.196	-0.021	-22.22	2.720	-0.029	-19.49
0.4657	3.691	-0.022	-26.98	3.198	-0.027	-25.13	2.699	-0.034	-22.61
0.5560	3.692	-0.026	-27.17	3.201	-0.029	-25.57	2.684	-0.036	-23.89
0.6577	3.697	-0.026	-26.03	3.208	-0.030	-24.11	2.669	-0.036	-23.05
0.7656	3.705	-0.024	-22.05	3.219	-0.026	-19.70	2.658	-0.031	-19.67
0.8805	3.719	-0.015	-13.29	3.237	-0.017	-11.92	2.652	-0.020	-10.63
1.0000	3.740	0.000	0.00	3.262	0.000	0.00	2.655	0.000	0.00
					ohol (1) + Benza				
0.0000	1.392	0.000	0.00	1.320	0.000	0.00	1.248	0.000	0.00
0.0930	1.815	0.205	75.32	1.679	0.178	65.00	1.504	0.125	64.44
0.1848	2.197	0.371	137.7	1.964	0.285	115.0	1.734	0.226	105.9
0.2816	2.524	0.471	170.9	2.257	0.390	152.1	1.956	0.311	129.5
0.3771	2.838	0.560	181.0	2.487	0.435	160.6	2.155	0.376	142.2
0.4926	3.142	0.593	171.6	2.752	0.475	152.1	2.332	0.390	135.0
0.5824	3.338	0.579	154.7	2.897	0.446	133.8	2.452	0.385	123.1
0.5824	3.508	0.515	127.8	3.059	0.415	114.7	2.536	0.329	99.60
0.8816	3.647	0.515	93.89	3.174	0.415	85.53	2.536	0.329	72.89
0.7844	3.718	0.233	49.24	3.241	0.190	46.56	2.641	0.139	39.85
1.0000	3.740	0.000	0.00	3.262	0.000	0.00	2.655	0.000	0.00
0.000	1 000	0.000	0.00		cohol (1) + Nitro		1.520	0.000	0.00
0.0000	1.809	0.000	0.00	1.659	0.000	0.00	1.529	0.000	0.00
0.0937	2.261	0.271	68.62	1.933	0.124	45.63	1.692	0.058	24.02
0.1861	2.570	0.401	112.9	2.181	0.224	73.97	1.855	0.117	42.36
0.2834	2.877	0.521	131.1	2.394	0.281	84.20	2.012	0.164	54.21
0.3791	3.150	0.609	138.6	2.594	0.327	89.20	2.150	0.195	59.46
0.4948	3.385	0.621	130.5	2.782	0.329	80.42	2.302	0.216	59.83
0.5845	3.539	0.601	114.2	2.912	0.316	71.17	2.398	0.212	55.08
0.6834	3.669	0.540	90.18	3.016	0.261	54.15	2.486	0.188	45.90
0.7859	3.739	0.412	60.66	3.136	0.218	41.12	2.567	0.154	35.34
0.8922	3.739	0.207	30.06	3.231	0.142	25.53	2.631	0.098	20.49
1.0000	3.740	0.000	0.00	3.262	0.000	0.00	2.655	0.000	0.00

The standard uncertainty components u for each variable are u(T)= ± 0.01 K, u(x) = $\pm 1 \times 10^{-4}$, $u(p)=\pm 1.0$ kPa, u(η) = $\pm 28 \times 10^{-3}$ m²/s and the combined expanded Uncertainty is $U(G^{*E} \times 10^3) = \pm 7 \times 10^{-1}$ N. mol⁻¹ at 0.95 level of confidence, respectively.

Table 5 Values of density (ρ) , speed of sound (u) and deviation in isentropic compressibility $(\Delta \kappa_s)$ for all the studied binaries at varying temperatures.

		T = 298.15	K	7	$\Gamma = 303.15$	K	-	$\Gamma = 308.15$	K
ΧIAA	10^{-3} . $\rho/$ (kg. m ⁻³)	u/ (m.s ⁻¹)	10 ¹¹ . $\Delta \kappa_s / (m^2. N^{-1})$	10^{-3} . ρ / (kg. m ⁻³)	u/ (m.s ⁻¹)	10 ¹¹ . $\Delta \kappa_s /$ (m ² . N ⁻¹)	10^{-3} . $\rho/$ (kg. m ⁻³)	u/ (m.s ⁻¹)	10 ¹¹ . $\Delta \kappa_s$ (m ² . N ⁻¹)
7(1111				l alcohol (1)			()	,	
0.0000	1.1001	1269.1	0.000	1.0955	1250.0	0.000	1.0896	1239.8	0.000
0.0933	1.0791	1265.7	-0.908	1.0724	1244.1	-0.829	1.0654	1227.7	-0.699
0.1853	1.0567	1264.4	-1.840	1.0510	1235.6	-1.371	1.0431	1215.1	-1.264
0.2823	1.0342	1261.2	-2.651	1.0280	1229.1	-2.061	1.0190	1204.2	-1.915
0.3778	1.0091	1259.4	-3.334	1.0027	1222.7	-2.461	0.9930	1193.1	-2.192
0.4934	0.9798	1253.1	-3.675	0.9713	1214.8	-2.694	0.9605	1182.3	-2.503
0.5832	0.9539	1249.1	-3.719	0.9450	1209.7	-2.701	0.9341	1174.2	-2.479
0.6822	0.9231	1245.5	-3.530	0.9137	1205.7	-2.491	0.9032	1167.0	-2.294
0.7849	0.8880	1240.2	-2.701	0.8798	1201.2	-1.978	0.8688	1160.8	-1.767
0.8917	0.8481	1237.1	-1.520	0.8411	1199.3	-1.130	0.8331	1155.3	-0.997
1.0000	0.8070	1235.0	0.000	0.8030	1197.3	0.000	0.7969	1151.0	0.000
1.0000	0.0070	1233.0		nyl alcohol (1			0.7505	1151.0	0.000
0.0000	1.0008	1592.4	0.000	0.9963	1582.2	0.000	0.9918	1570.6	0.000
0.0000	0.9917	1551.7	-1.452	0.9867	1532.7	-1.344	0.9812	1510.2	-1.243
0.1863	0.9809	1515.3	-2.802	0.9737	1485.0	-2.238	0.9677	1455.8	-2.146
0.2836	0.9706	1471.2	-3.674	0.9606	1442.8	-3.354	0.9526	1405.6	-3.015
0.3794	0.9560	1435.4	-4.514	0.9450	1400.3	-3.876	0.9370	1358.3	-3.459
0.4953	0.9354	1391.1	-4.887	0.9248		-4.293	0.9370		-3.439
0.5848	0.9354	1359.0	-4.828	0.9248	1354.1 1320.2	-4.293 -4.172	0.8970	1308.2 1274.4	
									-3.722
0.6837 0.7861	0.8950 0.8699	1326.3 1293.2	-4.496 -3.559	0.8856 0.8600	1286.7 1255.4	-3.872 -3.085	0.8746 0.8508	1239.9 1208.5	-3.316 -2.723
0.8924	0.8409	1260.5	-1.902	0.8332	1222.5	-1.529	0.8249	1177.3	-1.462
1.0000	0.8070	1235.0	0.000 Iso	0.8030 amyl alcohol	1197.3 (1) + Anili	0.000 ne (2)	0.7969	1151.0	0.000
0.0000	1.0174	1637.8	0.000	1.0131	1619.3	0.000	1.0085	1595.3	0.000
0.0843	1.0104	1605.1	-1.989	1.0034	1575.6	-1.649	0.9950	1543.3	-1.466
0.1691	1.0002	1561.3	-3.172	0.9941	1525.3	-2.733	0.9790	1490.1	-2.387
0.2604	0.9870	1515.7	-4.158	0.9802	1480.5	-3.916	0.9642	1438.5	-3.357
0.3521	0.9715	1475.1	-5.047	0.9625	1431.8	-4.300	0.9491	1384.3	-3.612
0.4657	0.9493	1421.8	-5.310	0.9401	1377.7	-4.529	0.9271	1328.0	-3.770
0.5560	0.9290	1384.2	-5.269	0.9204	1338.1	-4.338	0.9088	1287.3	-3.565
0.6577	0.9056	1343.4	-4.798	0.8966	1298.5	-3.875	0.8861	1245.5	-2.884
0.7656	0.8780	1304.3	-3.847	0.8691	1258.8	-2.719	0.8603	1210.6	-2.338
0.8805	0.8447	1266.2	-2.083	0.8378	1225.5	-1.516	0.8281	1177.9	-1.022
1.0000	0.8070	1235.0	0.000	0.8030	1197.3	0.000	0.7969	1151.0	0.000
1,0000	0.0070	123010		yl alcohol (1)			0.7000	110110	0.000
0.0000	1.0442	1460.3	0.000	1.0356	1452.2	0.000	1.0312	1442.1	0.000
0.0930	1.0386	1453.0	-2.683	1.0270	1430.3	-2.013	1.0191	1410.9	-1.809
0.1848	1.0274	1435.3	-4.378	1.0127	1411.7	-3.832	1.0020	1384.7	-3.466
0.2816	1.0118	1413.6	-5.685	1.0002	1381.8	-4.994	0.9866	1346.5	-4.270
0.3771	0.9941	1388.4	-6.427	0.9821	1353.3	-5.680	0.9671	1314.7	-4.938
0.4926	0.9680	1356.5	-6.671	0.9554	1318.5	-5.821	0.9424	1275.3	-5.077
0.5824	0.9454	1331.7	-6.432	0.9340	1290.4	-5.417	0.9214	1246.4	-4.778
0.6816	0.9171	1306.1	-5.757	0.9066	1263.9	-4.740	0.8966	1216.7	-4.065
0.7844	0.8860	1279.2	-4.441	0.8751	1238.7	-3.537	0.8671	1190.1	-2.926
0.8914	0.8491	1254.8	-2.505	0.8401	1215.5	-1.840	0.8307	1170.4	-1.619
1.0000	0.8070	1235.0	0.000 Isoam	0.8030 yl alcohol (1)	1197.3 + Nitrobe	0.000 nzene (2)	0.7969	1151.0	0.000
0.0000	1.1971	1461.0	0.000	1.1913	1413.2	0.000	1.1862	1423.1	0.000
0.0937	1.1812	1452.8	-2.974	1.1702	1399.3	-2.593	1.1601	1390.5	-2.021
0.1861	1.1570	1435.5	-5.032	1.1463	1375.8	-4.289	1.1350	1361.3	-3.965
0.2834	1.1308	1411.7	-6.698	1.1181	1347.7	-5.496	1.1037	1323.5	-4.949
0.3791	1.1008	1383.9	-7.671	1.0865	1321.3	-6.313	1.0700	1288.7	-5.480
0.4948	1.0593	1346.7	-7.924	1.0456	1287.3	-6.508	1.0267	1251.4	-5.704
0.5845	1.0234	1320.4	-7.711	1.0094	1264.6	-6.297	0.9900	1224.6	-5.307
0.6834	0.9780	1292.0	-6.664	0.9658	1243.1	-5.671	0.9472	1199.2	-4.497
0.7859	0.9287	1270.2	-5.494	0.9171	1221.2	-4.153	0.9007	1179.0	-3.478
0.8922	0.8719	1248.6	-3.147	0.8612	1210.3	-2.769	0.8512	1162.1	-2.006
1.0000	0.8070	1235.0	0.000	0.8030	1197.3	0.000	0.7969	1151.0	0.000

The standard uncertainty components u for each variable are u(T)= ± 0.01 K, u(x) = $\pm 1 \times 10^{-4}$, $u(p)=\pm 1.0$ kPa, u(ρ) = $\pm 2 \times 10^{-2}$ g.cm⁻³. u(u)=0.5% and the combined expanded Uncertainty is $U(\Delta\kappa_s\times 10^{11})=\pm 3\times 10^{-2}$ m². N⁻¹ at 0.95 level of confidence, respectively.

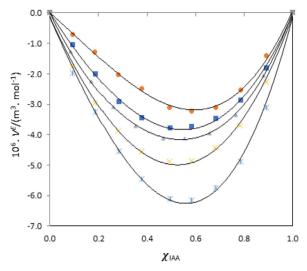


Fig. 1. Variation of V^E of the as a function of mole fraction of IAA at 298.15 K: •, {IAA (1) + CB (2)}; •, {IAA (1) + BN (2)}; •, {IAA (1) + NB (2)}; *, {IAA (1) + NB (2)}.

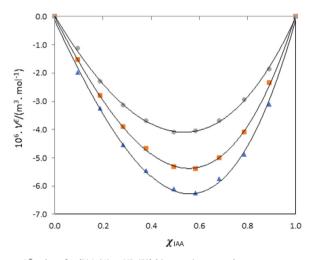


Fig. 2. Plot of mole fraction of IAA versus V^E values for {IAA (1) + NB (2)} binary mixture at three temperatures: \blacktriangle , 298.15 K; \blacksquare , 303.15 K; \bullet , 308.15 K.

dipole-dipole interactions when the addition of solvent with co-solvent components [18,19], (ii) intermolecular forces raised when two-component molecules come close to each other [20], (iii) if molecules having difference in size, shape, and structure, the steric hindrance produced between heterogeneous molecules [21], (iv) electrostatic repulsions formed when mixing of unlike polar solvents, and (v) unfavorable geometric fitting [22]. The above factors (i to v) leads to an expansion in the volume of the binary mixtures. The negative V^E phenomenon was due to the following reasons: (i) electron-transfer in mixing components when the dipole-dipole interactions mixing of liquid unlike molecules [23], (ii) electron donor-acceptor complexes formed when the dipole-induced dipole interaction of mixed components, (iii) the formation of intermolecular hydrogen bonds of the two different kinds of molecules [24], (iv) packing effect between molecules when the size of molecules were also different [25], (v) complex formation due to interaction between acid and base molecules, and (vi) the dielectric constants of the mixtures liquid components [26]. The above points (i to vi) leads to a contraction in the volume of the non-ideal binary mixtures.

The values of V^E for all the examination binaries plotted against the mole fraction of isoamyl alcohol is fitted in Fig. 1 at a constant temperature 298.15 K. From this fig. illustrates that the curves of V^E for the reported solutions are negative deviation from ideal solutions, and the absolute value of the excess volume showed that the firstly increased and then decreased throughout all the range of mole fraction of IAA when the temperature was constant [27]. In unlike molecules, molecular interactions increase with V^E increases in negative values. The negative V^E of selected binary mixtures (IAA + BMSC) due to working of the following factors:

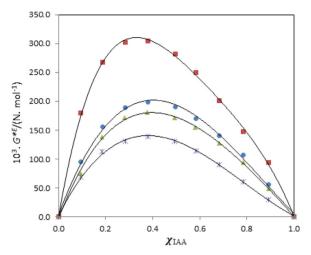


Fig. 3. Variation of G^{*E} of the as a function of mole fraction of IAA at 298.15 K: ■, {IAA (1) + CB (2)}; •, {IAA (1) + BN (2)}; ▲, {IAA (1) + BZ (2)}; *, {IAA (1) + NB (2)}.

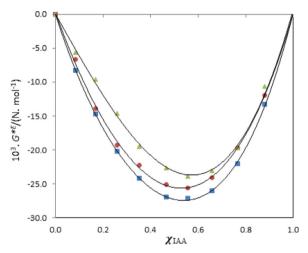


Fig. 4. Plot of mole fraction of IAA versus G^{*E} values for {IAA (1) + AL (2)} binary mixture at three temperatures: \blacksquare , 298.15 K; \bullet , 303.15 K; \triangle , 308.15 K.

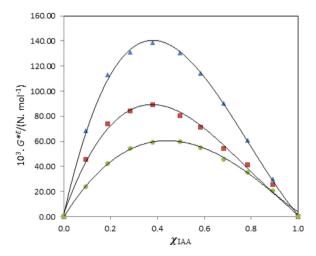


Fig. 5. Plot of mole fraction of IAA versus G^{*E} values for {IAA (1) + NB (2)}binary system at three temperatures: \blacktriangle , 298.15 K; \blacksquare , 303.15 K; \bullet , 308.15 K.

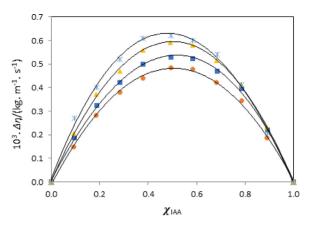


Fig. 6. Variation of $\Delta \eta$ of the as a function of mole fraction of IAA at 298.15 K: •,{IAA (1) + CB (2)}; ■, {IAA (1) + BN (2)}; ▲, {IAA (1) + BZ (2)}; *, {IAA (1) + NB (2)}.

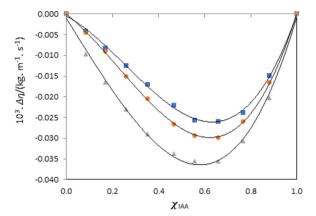


Fig. 7. Plot of mole fraction of IAA versus $\Delta \eta$ values for {IAA (1) + AL (2)} binarysystem at three temperatures: \blacksquare , 298.15 K; \bullet , 303.15 K, \bullet , 308.15 K.

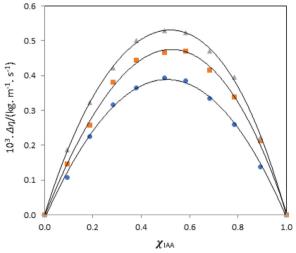


Fig. 8. Plot of mole fraction of IAA versus $\Delta \eta$ values for {IAA (1) + BN (2)} binarysystem at three temperatures: \blacktriangle ; 298.15 K, \blacksquare ; 303.15 K, \bullet ; 308.15 K.

- (i) Breaking effect (especially in AL); if mixing of unlike components immediately breaking of bonds (intra-hydrogen bonds, dipole-dipole bonds) in like molecules and formation of new bonds between unlike molecules [28].
- (ii) H-bonding effect (major contribution); inter-molecular hydrogen bonding formed between IAA and BMSC.
- (iii) Fitting effect; interstitial accommodation of molecules of one component into the vacant spaces of molecules of other components [29].
- (iv) The OH- π interactions.
- (v) Negative inductive effect.

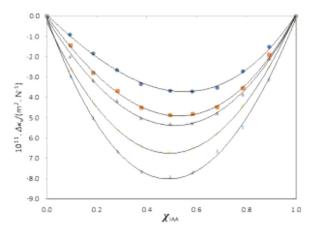


Fig. 9. Variation of $\Delta \kappa_s$ of the as a function of mole fraction of IAA at 298.15 K: •, {IAA (1)+ CB (2)}; ■, {IAA (1)+ BN (2)}; ▲, {IAA (1)+ AL (2)}; x, {IAA (1)+ BZ (2)}; *, {IAA (1)+ NB (2)}.

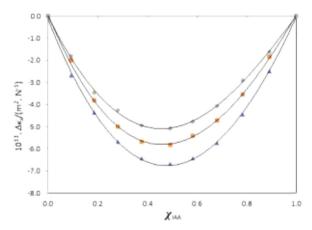


Fig. 10. Plot of mole fraction of IAA versus $\Delta \kappa_s$ values for {IAA (1) + BZ (2)} binarycomponent at three temperatures: \blacktriangle , 298.15 K; \blacksquare , 303.15 K; \bullet , 308.15 K.

From the analysis of the reported results in Table 3 and Fig. 1, it is observed that the contraction values of V^E fall in the order at 298.15 K and studied temperatures;

 $(C_5H_{12}O + C_6H_5CI) > (C_5H_{12}O + C6H_5(CN)) > (C_5H_{12}O + C_6H_5NH_2) > (C_5H_{12}O + C_6H_5CHO) > (C_5H_{12}O + C_6H_5NO_2)$

The series of the above V^E values are maybe the presence of different types of interaction (intermolecular interaction) abilities of molecules of IAA with molecules of BMSC. The strong intermolecular interactions (more negative V^E) are observed in the type of system (IAA + NB) due to the following reasons; (a) H-bonding interactions: this bond possible in two ways the first one is (NB)N•••H-O(IAA) type and (NB)O••• H-O(IAA) (more favorable bond due to oxygen have extra electronegative compared to nitrogen) second type hydrogen bonding formed between IAA and NB molecules [30]. (b) OH- π interactions: nitrobenzene has six π - electron cloud at set distance that are delocalized over the ring, OH- π interaction produced between -OH (positive charge on H atom) part of IAA and π -electrons of NB, and this interaction much weaker than H-bonding interaction because of more negative induct effect on benzene ring through nitro group. Due to the negative induct effect of NO₂ group, the π electrons in the benzene ring partially moved to the nitro group and electron density less in-ring automatically weak OH- π interactions. (c) fitting interactions (very less): NB molecule having less space for geometrical fitting to IAA molecules. The IAA volume progressively decreases when IAA added with NB due to molecules very closeness and this closeness of molecules explained based on above mentioned (a, b and c) interactions. The small negative V^E values observed in IAA + CB mixtures indicate the prevalence of weak structure-making interactions. When chlorobenzene is mixed with isoamyl alcohol, chlorinated benzene can interact with the -OH group, the form of (CB)Cl • • • H-O(IAA) weak intermolecular hydrogen bonding and Cl • • •O electron acceptor-donor interaction [31]. Further, the molar volumes

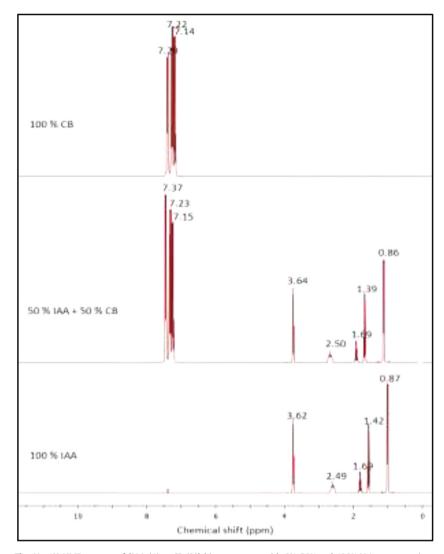


Fig. 11. 1H-NMR spectra of $\{IAA\ (1)+CB\ (2)\}$ binary system with 0%, 50% and 100% IAA concentrations.

of IAA and CB at 298.15 K are (102.32 and 109.23) cm³. mol⁻¹ respectively. A smaller molar volume difference between IAA and CB would allow a less favorable fitting of molecules into the spaces created by IAA molecule and Additionally, OH- π interactions observed. The molecules closeness very less compared to other studied binaries due to weak interactions in CB + IAA system. The V^E values of IAA + BN, + AL and + BZ systems are more than mixture of IAA + CB and less than IAA + NB solution. The molecule closeness (intermolecular interaction) decreasing order; IAA + {NB > BZ > AL > BN > CB}. Earlier, the negative values of the excess volume had been reported by Karunakar et al. [32] and Fialkov and Fenerli [33] for the binary liquid mixtures of isoamyl alcohol with benzonitrile and for the binary solutions of isoamyl alcohol with benzaldehyde. Our results of V^E show more negative values compared with literature values for the IAA + BN, + BZ systems due to the high purity of solvents (less impurities) were used and which result more negative values were observed. More negative V^E values indicate that strong intermolecular interactions in unlike molecules.

The effect of temperature on excess volume for (IAA + NB) system is typically shown in Fig. 2 and it is observed that negative V^E values decrease systematically with increases temperature from T = 298.15 K to 308.15 K [34]. The negative V^E values decreasing means molecule closeness (MC) gradually decreasing between solvent and co-solvent molecules. This phenomenon recommends that, with a rise in the temperature, the molecules gotten in the form of heat energy and which results in the molecules move a long distance from each other and therefore the less negative V^E values obtained due to molecules closeness decreases. The MC decreasing order of the IAA + NB system at variable temperatures: [MC]_{298.15 K} > [MC]_{303.15 K}. The similar trend is also observed in other studied binaries.

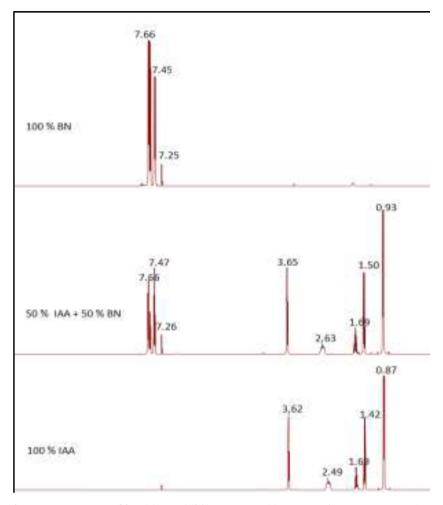


Fig. 12. 1H-NMR spectra of {IAA (1) + BN (2)} binary system with 0%, 50% and 100% IAA concentrations.

3.2. Excess Gibbs free energy

By using the experimental data viscosity of pure liquids, binary mixtures and corresponding mole fractions the excess Gibbs free energy (G^{*E}) for viscous flow was computed using the relation [35];

$$G^{*E} = RT \left[\ln(V_m \eta_m) - \sum_{i=1}^2 x_i \ln(V_i \eta_i) \right]$$
(6)

where,

 V_m = molar volume of the added mixtures,

 V_i = molar volume of pure components,

R = ideal gas constant, and T = absolute temperature.

The calculated C^{*E} data for the five different unlike component binary mixtures such as IAA + chlorobenzene, + benzonitrile, + aniline, + benzaldehyde and + nitrobenzene at temperatures T = 298.15 K, 303.15 K, and 308.15 K are tabulated in Tables 4 and graphically depicted in Figs. 3–5. This excess function from Figs, it can be observed that of the IAA + AL system are of negative deviation and the remaining binary mixtures are of positive deviations from ideal behavior at a certain temperature. The magnitude of C^{*E} represents the power of intermolecular interactions when mixing of IAA with BMSC [36,37]. The negative curves of C^{*E} represent the presence of weak/no interactions such interaction is the dominance of the dispersion type of forces in the mixtures under study [38]. The positive curves of C^{*E} indicate the presence of strong interactions (H-bond interaction and OH- π interaction) and molecule's accommodation interactions in the mixtures under investigation [39]. The negative values of C^{*E} are obtained when mixture flow is easier compared with that of pure liquids and if the flow of solution is hardly when compared with that of pure component and therefore, positive values of C^{*E} are produced under examination. It can be observed from Figs. 3 and 4, the values of C^{*E} for all investigated binaries;

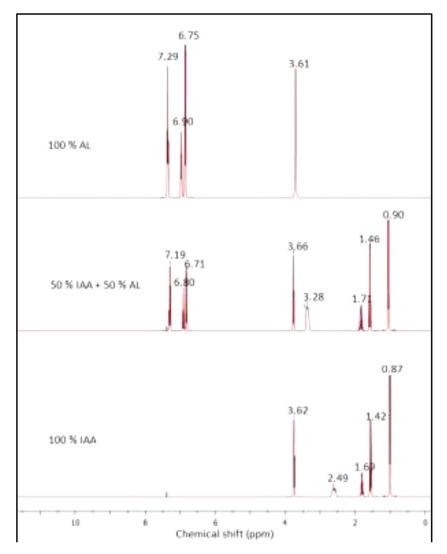


Fig. 13. 1H-NMR spectra of {IAA (1) + AL (2)} binary system with 0%, 50% and 100% IAA concentrations.

[IAA + CB] > [IAA + BN] > [IAA + BZ] > [IAA + NB] > 0 > [IAA + AL]

From above sequence of G^{*E} have been given that, the IAA + CB system having more positive value due to flow of that mixture is very slow compared with IAA solution but in IAA + AL system having negative value observed because of this mixture flow is easier compared with all studied two component mixtures. The viscous flow of mixtures was given an orderly: CB < BN < BZ < NB < AL.

It can be observed, the negative values of negative G^{*E} decrease with increases of temperature from 298.15 to 308.15 K for the IAA + AL mixture shown in Fig. 4 [40] and the positive values of G^{*E} decrease with increases in range of studied temperature for NB system (Fig. 5) and remaining binaries at a constant mole fraction of IAA [41]. The values of G^{*E} decrease when temperature increasing from 298.15 to 308.15 K due to possibly the breaking of inter-molecular hydrogen bonding interactions between the unlike chemical species present in the studied solutions.

3.3. Deviation in viscosity

The deviation in viscosity was calculated from using experimental viscosity data of similar or dissimilar binary systems, and according to Eq. 7 [42];

$$\Delta \eta = \eta_{\rm m} - \sum_{i=1}^{2} (x_i \eta_i) \tag{7}$$

here, η_m = viscosity of the multicomponent mixtures and η_i = viscosities of pure components, respectively.

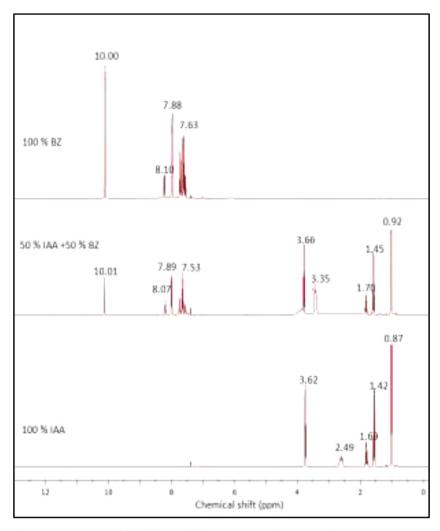


Fig. 14. 1H-NMR spectra of $\{IAA(1) + BZ(2)\}$ binary system with 0%, 50% and 100% IAA concentrations.

The $\Delta\eta$ is a function of the intermolecular interactions as well as of the molecular geometry and size. Therefore, the magnitude of this deviation from the ideal behavior of the binary component systems can be positive, negative or zero. The results of $\Delta\eta$ values were placed in Table 4. Fig. 6 represents the viscosity deviation of four binary systems such as IAA (1) + CB (2), IAA (1) + BN (2), IAA (1) + BZ (2) and IAA (1) + NB (2) has positive deviations from ideality and whereas, IAA (1) + AL (2) mixture has negative deviation (Fig. 7) from ideal axis for throughout mole fraction of IAA at a constant temperature 298.15 K. The positive deviation obtained from ideality it takes place in different manners [43,44]: namely (i) H-bonding interaction occurred between dissimilar molecules, (ii) OH- π interactions between opposed molecules, (iii) molecules geometrically fixed inside molecules of other compounds, (iv) charge transfer complex formation, etc. whereas viscosity deviation is negative when without strong intermolecular interactions occurred in mixture molecules, these interactions such as dipole-dipole, H-bonding rupture and dispersion force [45]. Generally, the deviation of $\Delta\eta$ was found to be inverse to the deviation of V^E for all examination binary unlike molecules. This phenomenon was satisfactory by Brocal et al. [46], Mrad et al. [47], Dubey et al. [48], and Roy et al [49]. From the number of binary real solutions, a correlation between the variation of curves of V^E and $\Delta\eta$ has been detected; if V^E is a negative isotherm whereas $\Delta\eta$ is a positive isotherm and vice-versa [50]. The IAA + AL system is not satisfactory above the phenomenon. The deviation of $\Delta\eta$ rise in the order for the mixture of IAA with BMSC at 298.15 K, also at 303.15 K and 308.15 K temperatures.

 $(\Delta \eta)_{AL} < 0 < (\Delta \eta)_{CB} < (\Delta \eta)_{BN} < (\Delta \eta)_{BZ} < (\Delta \eta)_{NB}$

A qualitative explanation of the non-ideal behavior of the above series with composition of IAA may be suggested. Adding of the solvent with co-solvent will induce (i) the interruption of H- bonds in IAA, AL, and loss of dipolar association in CB, BN, BZ and NB molecules, (ii) the formation of weak H-bonds between π -electron density of aromatic rings (all studied co-solvent molecules) and H-atom of the IAA molecule, whereas strong H-bonds between the components in the mixtures and

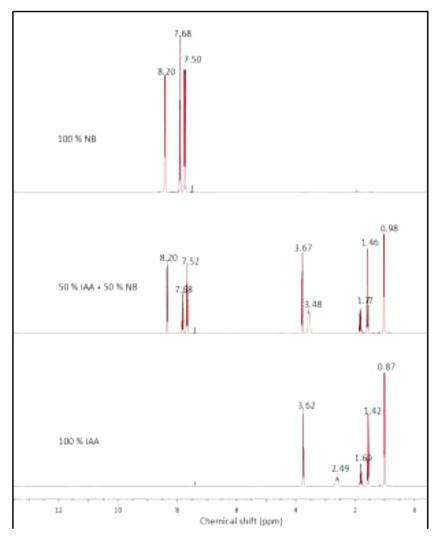


Fig. 15. 1H-NMR spectra of {IAA (1) + NB (2)} binary mixture with 0%, 50% and 100% IAA concentrations.

these two types of bonds further depend on function groups are present on benzene ring. The more positive values of $\Delta \eta$ (Fig. 6) for the combinations of IAA (1) + NB (2) propose the presence of comparatively strong intermolecular interactions between the IAA and NB molecules, which might be of H-bonds

 $(N \cdot \cdot \cdot H-O, O \cdot \cdot \cdot H-O, and OH-\pi)$ and molecules fitting interaction types [51]. This suggests that the mixture tends towards maximum non-ideal behavior from ideal axis. The small positive values of $\Delta \eta$ for system of IAA (1) + CB (2) due to weak (less electronegative) CI···H-O bond formed between them compared to other systems. Which indicates that the system tends towards ideal behavior. The IAA (1) + BZ (2) system having strong H-bond (O···H-O) intermolecular interactions compared with IAA (1) + BN (2) mixture (N···H-O type bond) due to O atom has more electronegative compare with N atom. These two systems have been intermediate interactions between NB and CB systems. On the other hand, the negative $\Delta \eta$ values of the IAA (1) + AL (2) (Fig. 7) system were obtained due to the existence of weak dispersion forces [5] and which represent that less thickness solution mixtures are formed than other studied binaries.

From Fig. 8 (IAA (1) + BN (2) composition), it is seen that $\Delta\eta$ are positive for at temperature range 298.15 to 308.15 K and a constant mole fraction of IAA. The obtained results show that $\Delta\eta$ decrease (less positive) with the rise of selected temperature range and thus, telling the intermolecular interactions in molecules become very weaker with increasing temperature and making their flow easier (less thickness of solution) with lower viscosity [52]. This indicates that with increase in temperature the system tends to ideal behavior. the thickness (T) of solution (BN system) decreasing order at different temperatures: $[T]_{298.15 \text{ K}} > [T]_{303.15 \text{ K}} > [T]_{308.15 \text{ K}}$. The similar behavior of IAA + CB, + BZ and + NB systems are shown under study.

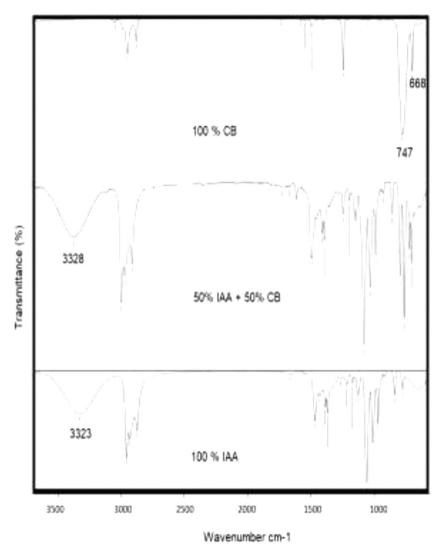


Fig. 16. FT-IR spectra of $\{IAA(1) + CB(2)\}$ binary system with 0%, 50% and 100% IAA concentrations.

3.4. Deviation in isentropic compressibility

The isentropic compressibility (κ_s) of the pure substance and their binary mixtures and deviation in isentropic compressibility $(\Delta \kappa_s)$ were computed according to the following equations [53,54] using the experimentally measured ρ and u data;

$$\kappa_{\rm S} = \frac{1}{\rho u^2} \tag{8}$$

$$\Delta \kappa_s = \frac{1}{\rho u^2} - \sum_{i=1}^2 \frac{\kappa_i}{\rho_i u_i^2} \tag{9}$$

here,

 κ_s = isentropic compressibility of adding compositions,

 ρ_i = density of pure components and u_i = speed of sound of pure substances,

 ρ and u = density and speed of sound of multicomponent mixtures, respectively.

For all studied binaries, the calculated values of $\Delta \kappa_s$ are given in Table 5 at temperatures 298.15, 303.15 and 308.15 K. The obtained results are exhibit in Fig. 9 and which represent that $\Delta \kappa_s$ values are negative over the entire mole fraction range of IAA and at a constant temperature 298.15 K examined for each binary system under study. This indicates that increase in the compressibility (volume contraction) of the mixtures moves from chlorobenzene to nitrobenzene. Further, it suggests that change in the IAA molecule structure with the addition of CB, BN, AL, BZ and NB molecules due to compressibility

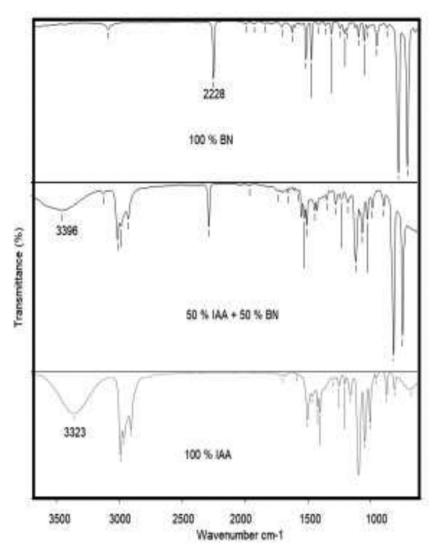


Fig. 17. FT-IR spectra of $\{IAA(1) + BN(2)\}$ binary mixture with 0%, 50% and 100% IAA concentrations.

of the mixture increase [55]. The magnitude of negative $\Delta \kappa_s$ values (Fig. 9) at equimolar composition of these systems at temperature 298.15 K follows the direction:

$[\Delta \kappa_s]_{CB} < [\Delta \kappa_s]_{BN} < [\Delta \kappa_s]_{AL} < [\Delta \kappa_s]_{BZ} < [\Delta \kappa_s]_{NB}$

From the above order, it is understood that the strength of the intermolecular interactions in studied unlike molecules are estimated in terms of plausible interactions. The more negative $\Delta \kappa_s$ values observed for IAA + BN than those IAA + CB. The plausible explanation maybe, when mixing of IAA with BN and CB will induce (i) the interruption of hydrogen bonds in IAA and loss of dipolar association in CB and BN molecules present in pure liquids, (ii) formation of strong H-bond (H...,N) between H-atom of the IAA molecule and nitrogen atom of BN (with its lone pair of electrons) and the chlorine atom of CB, being less electronegative compared with nitrogen atom, forming weak (H...Cl) bond due to presence of nitrile (-CN) group which has more -I effect at benzene ring increase the electron density at nitrogen atom in benzonitrile to greater extent, resulting stronger intermolecular interaction (H-bond) than that in chlorobenzene which has less -I effect chlorine atom. Also, the more negative $\Delta \kappa_s$ values obtained for IAA + AL than those for IAA + BN, are because in aniline presence of amino (NH₂) group two types of H-bonds take place which are (H-N•••••+H-O and N-H•••••O-H) between amino group of aniline and hydroxyl group of IAA molecules, resulting stronger inter-molecular interaction (H-bond) in aniline system compare with benzonitrile system due to more number of H-bonds possible with aniline system [56]. Further, the more negative $\Delta \kappa_s$ values gotten for IAA + BZ than those for IAA + AL understudy, because of this type of results forming stronger H-bond (H...O) in benzaldehyde than aniline system and which is explanation based on two factors; (i) oxygen atom in BZ has more electronegative than those of nitrogen atom in AL molecule, (ii) -CHO group in BZ has more -I effect compare with amine (NH₂) group in AL system. Furthermore, the large negative $\Delta \kappa_s$ values obtained for IAA + NB than

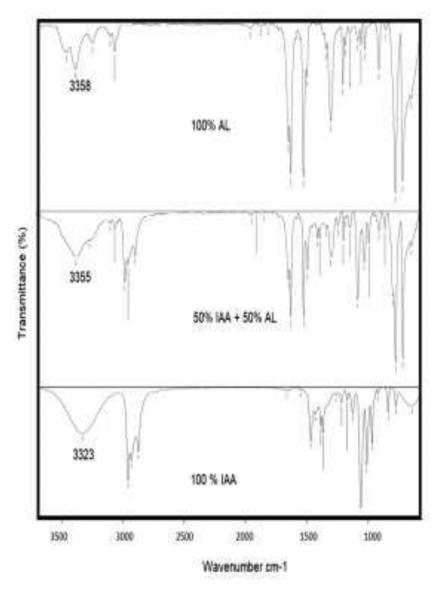


Fig. 18. FT-IR spectra of $\{IAA(1) + AL(2)\}$ binary mixture with 0%, 50% and 100% IAA concentrations.

those for IAA +BZ and other systems under investigation due to two types of hydrogen bonds (0....H-O and N....O-H) possible in NB but one type of hydrogen bond (0....H-O) forming in BZ. On the other type intermolecular interaction, for all binaries, there would be the formation of weak H.... π bond between H-atom of -OH group of IAA and π -electrons of benzene rings of co-solvents.

Previously, J. Karunakar et al. [57] had been reported the negative $\Delta \kappa_s$ values for the binary mixtures of isoamyl alcohol with benzonitrile T=308.15 K. Our results of $\Delta \kappa_s$ confirmation that large negative values were observed compared with literature values for the IAA + BZ system because of less impurities components were used.

The values of negative $\Delta \kappa_s$ decrease with increases in temperature from 298.15 to 308.15 K for the IAA + BZ mixture (Fig. 10) at a constant mole fraction of IAA under study. When the rise in selected temperature range the molecules in solution gain thermal energy and move to long-distance each other, leading to the breaking of H-bonded associates between unlike molecules [52]. Hence, a decrease in the compressibility of the mixture resulting in a decrease in negative $\Delta \kappa_s$ values. The compressibility [C] of solution (BZ system) decreasing sequence at different temperatures: $[C]_{298.15 \text{ K}} > [C]_{303.15 \text{ K}} > [C]_{308.15 \text{ K}}$. The similar behavior is shown for remaining four systems at studied temperatures under examination.

Furthermore, the formation of new chemical species between IAA and studied co-solvents through H-bonding, OH- π and molecules fitting interactions were observed. The molar volumes difference between studied common and non-common molecules was less and which results less favorable of one molecule fit into another molecule voids [22]. Therefore,

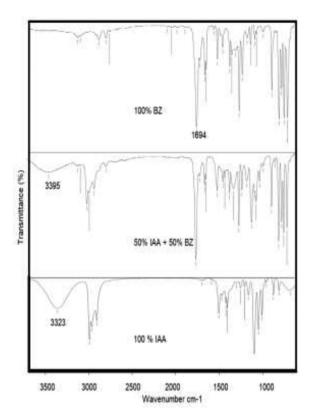


Fig. 19. FT-IR spectra of $\{IAA(1) + BZ(2)\}$ binary mixture with 0%, 50% and 100% IAA concentrations.

molecules fitting interaction was less compared to other interactions. All investigated co-solvents were contained π electrons density inside the benzene ring and monosubstituted groups on benzene. The formation of non-covalent bond interaction between H atom of OH in IAA and π electron density of the benzene ring. This interaction was weak in studied mixtures due to the negative induct effect groups on benzene ring and which effect π electrons in the benzene ring partially moved to induct effect groups. The IAA associated with CB, BN, AL, BA and NB through H-bonding interaction. Because of groups on benzene had been more electronegative atoms such as nitrogen, oxygen and chlorine, resulting in H-bonding interaction was strong compared to other interactions. These three interactions in studied binary solutions were agreed with interactions in A. Anwer and M. Tariq [51]. The intermolecular interactions in investigated unlike molecules as follows:

H-bonding interaction > OH- interaction > molecules fitting interaction

3.5. Standard deviations

The values of V^E , $\Delta \eta$ and $\Delta \kappa_S$ can be correlated well with the Redlich-Kister (R-K) Eq. 10 [58];

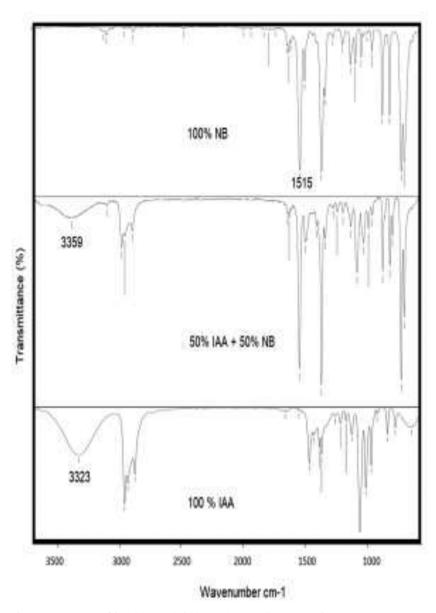
$$Z = x_1 x_2 \sum_{i=0}^{4} A_i (2x_i - 1)^i$$
 (10)

where Z represents V^E , $\Delta \eta$ and $\Delta \kappa_s$ are fitting functions based on the least-squares method, and A_0 , A_1 , A_2 , A_3 , and A_4 represent the adjustable binary coefficients. The coefficients A_i is calculate using multi-parametric regression analysis based on a non-linear least-squares method.

The corresponding standard deviations, σ (Z) were computed using the following relation [59].

$$\sigma(F(x)) = \left[\sum \left(Z_{exptl} - Z_{calcd}\right)\right]^2 / (p - n)^{1/2}$$
(11)

where, where P is the number of points of the sample and n is the number of free parameters of the fitting equation. The data analysis was performed using a fitting program Origin 8.0. Using Eq. 11, the accuracy of determination property can be compare obtained experimental results with calculated results at studied temperature. The calculated parameters A_i values along with the standard deviations (σ) are summarised in Tables 6–8. From obtained σ values it is found that the V^E , $\Delta \eta$ and $\Delta \kappa_S$ values for all studied binaries with lowest σ are correlated well by the Redlich–Kister (R-K) model.



 $\textbf{Fig. 20.} \ \ \text{FT-IR spectra of \{IAA\ (1)\ +\ NB\ (2)\}\ binary\ mixture\ with\ 0\%,\ 50\%\ and\ 100\%\ IAA\ concentrations.}$

3.6. ¹H-NMR spectra

¹H-NMR can provide meaningful physical information about structural and molecular interactions [60,61]. The ¹H-NMR chemical shift value is inversely proportional to the electron density around a proton. Interactions, such as the formation of hydrogen bonds between the different species present in a mixture or a change in their electronic environment, leads to changes in the chemical shift of the protons involved. The magnitude of these changes, and their relationship with the composition, provide information about what is happening at the molecular level [62].

The ¹H-NMR spectra of IAA (1) + CB (2), + BN (2), + AL (2), + BZ (2) and + NB (2) binary systems with 0%, 50% and 100% IAA concentrations were shown in Figs. 11–15. In pure IAA, the chemical shift at $\delta=2.49$ ppm (1H) was the H atom of the alcoholic group. The chemical shift of the hydrogen of the -CH₂-O- at $\delta=3.62$ ppm (2H), the chemical shift of the methylene group (-CH₂-) was present at $\delta=1.69$ ppm (2H), the chemical shift of methine group (-CH-) was present at $\delta=1.42$ ppm (H) and the chemical shift of the -CH₃ was present at $\delta=0.87$ ppm (3H). The proton chemical shift values of CB, BN, AL, BZ, and NB in pure states are given in Table 9.

Table 6 Coefficients $(A_0, A_1, A_2, A_3, \text{ and } A_4)$ of the Redlich-Kister Equation along with their standard deviations (σ) for excess volume (V^E) of all binary systems at T = 298.15 K, 303.15 K, and 308.15 K.

Binary system	T/K	Property	A_0	A_1	A_2	A_3	A_4	σ
IAA	298.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-10.90	-4.205	-11.95	-3.414	22.96	0.242
(1) + CB	303.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-9.422	-1.747	-14.39	-3.700	31.20	0.240
(2)	308.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-7.966	-0.164	-7.247	-4.243	16.58	0.197
IAA	298.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-14.20	-0.213	-8.868	-8.930	14.13	0.155
(1) + BN	303.15	10^6 . $V^E/$ (m ³ . mol ⁻¹)	-12.23	-1.632	-0.273	-1.629	1.135	0.064
(2)	308.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-10.76	-0.633	2.639	0.159	-3.985	0.022
IAA	298.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-16.38	-1.983	-5.056	-1.015	5.405	0.029
(1) + AL	303.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-14.18	-0.687	-6.131	-0.520	6.880	0.083
(2)	308.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-10.87	-3.414	-10.03	-1.332	23.98	0.166
IAA	298.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-19.84	-2.324	-0.307	0.924	-5.703	0.058
(1) + BZ	303.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-17.23	0.033	-3.493	-5.714	11.83	0.051
(2)	308.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-13.49	-3.791	-11.31	0.100	26.79	0.059
IAA	298.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-24.03	-4.599	-4.682	-5.302	1.977	0.096
(1) + NB	303.15	10^6 . $V^E/(m^3$. $mol^{-1})$	-20.01	-4.092	-11.21	-2.396	18.47	0.196
(2)	308.15	10^6 . $V^E/(m^3 \cdot mol^{-1})$	-15.32	-0.555	-6.253	-4.860	6.874	0.177

Table 7 Coefficients (A_0 , A_1 , A_2 , A_3 , and A_4) of the Redlich-Kister Equation along with their standard deviations (σ) for deviation in viscosity ($\Delta \eta$) of all binary mixtures at T=298.15 K, 303.15 K, and 308.15 K.

Binary system	Temp./K	Property	A ₀	A ₁	A ₂	A ₃	A ₄	σ
IAA	298.15	$10^3.\Delta\eta$ /(kg.m ⁻¹ . s ⁻¹)	1.868	0.112	0.569	0.004	-0.974	0.011
(1) + CB	303.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	1.737	0.111	-0.338	-0.136	0.066	0.012
(2)	308.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	1.638	0.160	0.221	-0.363	-2.099	0.009
IAA	298.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	2.127	0.201	0.346	-0.126	-0.319	0.008
(1) + BN	303.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	1.843	-0.119	0.514	1.070	-0.993	0.011
(2)	308.15	$10^3.\Delta \eta / (\text{kg.m}^{-1}.\text{ s}^{-1})$	1.475	-0.113	0.762	0.437	-1.677	0.017
IAA	298.15	$10^3.\Delta \eta / (\text{kg.m}^{-1}.\text{ s}^{-1})$	-0.080	-0.057	-0.129	-0.018	0.190	0.002
(1) + AL	303.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	-0.093	-0.051	-0.137	-0.048	0.222	0.003
(2)	308.15	$10^3.\Delta\eta / (kg.m^{-1}. s^{-1})$	-0.134	-0.043	-0.066	-0.018	0.061	0.001
IAA	298.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	2.382	0.143	-0.064	-0.453	0.472	0.007
(1) + BZ	303.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	1.933	0.078	-0.176	-0.128	0.364	0.014
(2)	308.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	1.550	-0.093	0.059	0.233	-0.497	0.006
IAA	298.15	$10^3.\Delta \eta / (\text{kg.m}^{-1}.\text{ s}^{-1})$	2.701	0.213	-1.183	-1.215	1.623	0.037
(1) + NB	303.15	$10^3.\Delta \eta / (kg.m^{-1}. s^{-1})$	1.370	-0.168	-0.568	0.041	1.509	0.009
(2)	308.15	$10^3.\Delta\eta\ /({\rm kg.m^{-1}.\ s^{-1}})$	0.804	-0.011	0.301	0.385	-0.405	0.010

Table 8 Coefficients (A_0 , A_1 , A_2 , A_3 , and A_4) of the Redlich-Kister Equation along with their standard deviations (σ) for deviation in isentropic compressibility ($\Delta \kappa_s$) of all binary solutions at T=298.15 K, 303.15 K, and 308.15 K.

Binary system	Temp./K	Property	A_0	A_1	A_2	A_3	A_4	σ
IAA	298.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-13.54	-1.723	-10.28	-4.717	20.68	0.229
(1) + CB	303.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-10.48	-0.808	-3.798	-3.687	9.415	0.060
(2)	308.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-9.411	-0.645	-4.623	-3.110	10.59	0.101
IAA	298.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-18.66	-2.546	-8.887	0.735	15.70	0.154
(1) + BN	303.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-16.48	-1.172	-8.992	-3.771	23.28	0.083
(2)	308.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-14.69	-0.837	-5.388	-1.649	11.13	0.044
IAA	298.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-22.72	-1.356	8.166	7.105	-11.88	0.232
(1) + AL	303.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-19.18	3.372	9.100	1.174	-10.34	0.208
(2)	308.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-16.00	3.182	6.014	3.447	-3.686	0.253
IAA	298.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-28.27	-0.405	9.439	7.959	-18.49	0.271
(1) + BZ	303.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-23.42	3.255	1.324	1.975	0.157	0.066
(2)	308.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-20.77	2.036	8.923	7.092	-17.16	0.081
IAA	298.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-32.72	1.163	3.405	-0.419	-7.870	0.194
(1) + NB	303.15	$10^{11}.\Delta\kappa_s/(m^2. N^{-1})$	-27.71	0.264	16.89	5.549	-37.39	0.255
(2)	308.15	$10^{11}.\Delta\kappa_s/(m^2.\ N^{-1})$	-23.03	3.047	5.359	4.247	-14.92	0.088

The relative changes of ¹H-NMR chemical shifts of -OH in pure IAA and their binary mixtures over the molar fraction range can be calculated as [63,64],

$$\Delta \delta = \delta_{mix} - \delta_{pur} \tag{12}$$

where δ_{mix} and δ_{pur} are the ¹H-NMR chemical shifts in the mixture and pure liquid (IAA), respectively. $\Delta\delta$ is the chemical shift change, which was calculated and listed in Table 10. The analysis of this property is interesting, once it provides

Table 9 $^1\text{H-NMR}$ chemical shifts δ (ppm) of different protons in benzene substituted components.

Component	δ (-H) $_{ m ortho}$	δ (-H) $_{ m meta}$	δ (-H) $_{ m para}$	$\delta(-NH_2)$	δ (-CHO)
СВ	7.29	7.14	7.22	_	_
BN	7.66	7.25	7.45	-	-
AL	6.75	7.29	6.90	3.61	-
BZ	8.10	7.63	7.88	-	10.0
NB	8.20	7.50	7.68	-	-

Table 10 1 H-NMR chemical shifts δ (ppm) of H atom of the hydroxyl in pure IAA and their binary systems.

System	Mole fraction of IAA	$\delta(\text{-OH})$	$\Delta\delta(\text{-OH})$
IAA	-	2.49	-
IAA + CB	0.4934	2.50	0.01
IAA + BN	0.4953	2.63	0.14
IAA + AL	0.4657	3.28	0.79
IAA + BZ	0.4926	3.35	0.86
IAA + NB	0.4948	3.48	0.99

Table 11 Experimental stretching frequency (cm⁻¹) of the alcoholic hydroxy group in pure IAA and change of stretching frequency after mixing of IAA in the pure solvents at equimolar composition.

System	Mole fraction of IAA	v(-OH)
IAA	-	3323
IAA + CB	0.4934	3328
IAA + BN	0.4953	3396
IAA + AL	0.4657	3355
IAA + BZ	0.4926	3395
IAA + NB	0.4948	3359

information concerning the solvent-co-solvent interactions between components present in binary solutions. Negative values of $\Delta\delta$ might be related to physical interactions between the components [65], while positive values may indicate the predominance of chemical interactions between the molecules [66,67]. Present studied all binaries given positive $\Delta\delta$ values and which indicate that H-bonding interaction between IAA and benzene substituted compounds.

From Table 10, it is clear that the chemical shift value of H atom of the alcoholic group for pure IAA (2.49 ppm) moved to the equimolar mixtures of IAA + CB (2.50 ppm), IAA + BN (2.63 ppm), IAA + AL (3.28 ppm), IAA + BZ (3.35 ppm) and IAA + NB (3.48 ppm) are observed. The sequence of the chemical shift changes of -OH proton of IAA with different cosolvents is $0 < \Delta \delta_{CB} < \Delta \delta_{BN} < \Delta \delta_{AL} < \Delta \delta_{BZ} < \Delta \delta_{NB}$ (Table 10). These sequences indicate that the magnitude sequence of the electron densities decrease in H atom of the hydroxyl is CB > BN > AL >BZ > NB. The increase in the chemical shift value of H atom of the hydroxyl when IAA mixing with studied co-solvents because of bond length of -O-H in IAA molecules becomes longer, the electron cloud of hydrogen atom of the alcoholic group in IAA molecules becomes thinner and the shielding effect of the hydroxyl hydrogen atom became weaker [68,69]. This result absorption peak shifted to the low field, and the chemical shift became higher due to alcoholic proton involved in hydrogen bond in studied unlike molecules.

3.7. FT-IR spectra

To scrutinize the molecular structure of association effects among molecules, FT-IR spectroscopy is a successful method. This technique offers the advantages to measure the association properties, to assess interactions by analyzing band shifts, shape, and hydrogen bonding capability. Two types of hydrogen bonds (inter and intramolecular) are readily distinguished by the FT-IR technique. Generally, intermolecular hydrogen bonds give rise to broad bands whereas bands arising from intramolecular hydrogen bonds are sharp bands [70].

Figs. 16–20 show that the FT-IR spectra of pure solvents and their equivalent mixtures with IAA over the entire range of mole fractions in the range of 400-4000 cm⁻¹. A broadband appears at 3323 cm⁻¹ for alcoholic hydroxy group in pure isoamyl alcohol. This is strong evidence for self-association of IAA involved in the H- bonding in the pure state [71]. When the composition of IAA is mixed to the equimolar composition of CB, BN, AL, BZ, and NB, the O–H stretching band of pure IAA shifted to 3328,3396, 3355, 3395 and 3359 cm⁻¹ in IAA + CB, + BN, + AL, + BZ and + NB binaries (Table 11). From the above interpretations, it can be determined that the intermolecular H-bonds in pure IAA molecule was broken gradually

by increasing the concentration of BMSC molecules and the –OH group of the IAA molecule is directly involved in the formation of H- bonding between component molecules [72], so that the absorption summit shifts to the high wavenumber direction. This implies that self-associated H-bond formation within pure IAA molecules decreases with increasing mass fraction of BMSC molecules.

4. Conclusions

In this article, the experimental data of densities (ρ), viscosities (η) and sound velocities (u) for the five non-ideal binary systems of {isoamyl alcohol + chlorobenzene, or + benzonitrile, or + aniline, or + benzaldehyde, or + nitrobenzene} have been measured as a function of composition at T=(298.15, 303.15, and 308.15) K at three equidistance temperature and atmosphere pressure. According to the experimental values, following excess and/or deviation parameters were calculated and fitted with using the Redlich–Kister (R-K) polynomial equation, as a function of mole fraction: excess volume (V^E), deviations in viscosity ($\Delta \eta$) and deviation in isentropic compressibility ($\Delta \kappa_s$) for examination systems. Negative deviations are observed in V^E and $\Delta \kappa_s$ values for all binary mixtures and which suggest for strong interactions. Positive deviations are observed in $\Delta \eta$ and G^{*E} values for all binary mixtures except for aniline. Further, the effect of different temperatures on thermodynamic parameters (V^E , $\Delta \eta$, G^{*E} , and $\Delta \kappa_s$) were studied. The excess /deviation parameters deviation from ideality were detected for the systems in terms of intermolecular interactions, and these interactions such as; (i) H-bonding interactions, (ii) OH- π interactions, and (iii) molecules fitting interactions between opposed molecules. To complement the thermodynamic results, FT-IR and 1 H-NMR spectroscopic analyses were carried out. The results suggest the predominance of H-bonding in studied unlike molecules.

Declaration of Competing Interest

None

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