



Acoustic And Thermodynamic Investigation Of Molecular Interactions In Selected Binary Liquid Mixtures At 303.15 K

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Abstract: A comprehensive acoustic and thermodynamic investigation has been carried out for three binary liquid mixtures, namely carbon tetrachloride-aniline, carbon tetrachloride-phenol, and methanol-acrolein, over the entire mole fraction range at 303.15 K. Ultrasonic velocity (U), density (ρ), and viscosity (η) were experimentally measured, and derived parameters such as adiabatic compressibility (β), volume expansivity (α), and their corresponding excess functions were evaluated to elucidate the nature and strength of intermolecular interactions. The carbon tetrachloride-aniline system exhibits moderate non-ideal behavior characterized by predominantly negative excess compressibility values, indicating dipole-induced dipole interactions and structural accommodation effects. In contrast, the carbon tetrachloride-phenol mixture shows positive excess compressibility across the composition range, suggesting disruption of strong phenol-phenol hydrogen bonding upon addition of nonpolar carbon tetrachloride. The methanol-acrolein system demonstrates pronounced negative excess functions at lower mole fractions, confirming strong specific interactions arising from heteromolecular hydrogen bonding between methanol hydroxyl groups and the carbonyl group of acrolein. Comparative analysis reveals that the interaction strength follows the order: Methanol-Acrolein > Carbon Tetrachloride-Aniline > Carbon Tetrachloride-Phenol. The study provides valuable insight into polarity-dependent molecular association, structural rearrangement, and deviation from ideal behavior in binary liquid mixtures.

Index Terms- Binary liquid mixtures, Ultrasonic velocity, Excess properties, Adiabatic compressibility, Molecular interactions, Hydrogen bonding.

I. INTRODUCTION

The investigation of molecular interactions in binary liquid mixtures has attracted considerable attention due to its importance in understanding thermodynamic non-ideality, solution structure, and transport behavior in chemical and industrial processes [1]. Intermolecular forces such as hydrogen bonding, dipole-dipole interactions, dipole-induced dipole interactions, and dispersion forces play a crucial role in determining macroscopic properties of liquid mixtures [2]. Several researchers have employed ultrasonic and thermodynamic studies to probe molecular interactions in liquid systems, as acoustic and volumetric parameters are highly sensitive to structural rearrangements and association phenomena at the molecular level [3]. Measurements of density, viscosity, and ultrasonic velocity, along with derived parameters such as adiabatic compressibility and volume expansivity, have been widely used to elucidate the strength and nature of interactions between unlike molecules in binary mixtures [4].

Binary mixtures composed of polar and nonpolar components exhibit diverse interaction mechanisms depending on the polarity, hydrogen-bonding capability, and molecular structure of the constituents [5]. In nonpolar-polar systems, the introduction of a nonpolar solvent tends to weaken the self-associated network of polar molecules, leading to structural modifications governed mainly by dispersion and dipole-induced dipole interactions [6]. Conversely, polar-polar mixtures are often characterized by strong specific

interactions such as hydrogen bonding and dipole-dipole attractions, resulting in significant deviations from ideal behavior [7]. Therefore, systematic experimental evaluation of acoustical and thermodynamic properties provides valuable insight into the extent of molecular association, structural effects, and interaction dynamics in such systems [8].

In this context, the present study focuses on three representative binary liquid mixtures: carbon tetrachloride-aniline, carbon tetrachloride-phenol, and methanol-acrolein over the entire mole fraction range. Carbon tetrachloride is a symmetric, nonpolar, and non-associating solvent dominated by dispersion forces [9], while aniline and phenol are polar aromatic compounds capable of dipole interactions, with phenol additionally exhibiting strong hydrogen bonding [10]. Methanol is a highly polar protic solvent forming extensive hydrogen-bonded networks [11], whereas acrolein is a polar unsaturated aldehyde capable of dipole-dipole and weak hydrogen-bond interactions through its carbonyl functional group [12]. The contrasting nature of these components makes these systems suitable models for investigating nonpolar-polar and polar-polar intermolecular interactions.

The variation of density and viscosity with mole fraction provides fundamental information about molecular packing, cohesive forces, and structural organization within the mixtures [13]. Ultrasonic velocity measurements enable the evaluation of adiabatic compressibility, which reflects the resistance of the medium to compression and is directly related to intermolecular free length and interaction strength [14]. Furthermore, derived thermodynamic parameters such as volume expansivity, excess adiabatic compressibility, and excess volume expansivity offer deeper insight into deviations from ideality and the extent of interaction between unlike molecules [15]. Positive or negative deviations in these excess properties reveal whether dispersive, associative, or structural effects dominate the mixture behavior [16]. Therefore, the objective of the present study is to systematically investigate the nature and strength of molecular interactions in carbon tetrachloride-aniline, carbon tetrachloride-phenol, and methanol-acrolein binary mixtures by analyzing mole fraction dependent density, viscosity, ultrasonic velocity, adiabatic compressibility, volume expansivity, and their corresponding excess parameters, in order to elucidate the interaction mechanisms and structural effects governing these liquid systems.

II. Results and discussion

II.i. Carbon Tetrachloride + Aniline (Nonpolar + Polar) System

The variation of ultrasonic velocity, density, adiabatic compressibility and volume expansivity with mole fraction indicates significant changes in molecular packing and interaction strength across the entire composition range (Fig. 1; Table 1). The ultrasonic velocity increases steadily from 903.22 ms^{-1} at pure carbon tetrachloride to 1589.26 ms^{-1} at pure aniline, suggesting enhancement in cohesive forces and closer molecular association with increasing aniline concentration. Simultaneously, density shows a gradual decrease up to intermediate mole fractions followed by minor irregularity, reflecting structural rearrangement and packing effects in the mixture.

The adiabatic compressibility decreases continuously with mole fraction, indicating increased resistance to compression and hence stronger effective intermolecular interactions at higher aniline content. This trend supports the formation of dipole-induced dipole interactions between nonpolar carbon tetrachloride and polar aniline molecules.

The excess adiabatic compressibility values are predominantly negative over most of the composition range, except near equimolar region where slight positive deviation is observed. Negative β^E values reveal stronger heteromolecular interactions compared to the pure components, confirming the presence of specific interaction and compact structure formation. Similarly, excess volume expansivity (α^E) shows both negative and positive deviations, suggesting competing effects of structural fitting and dispersion forces. Overall, the system exhibits moderate non-ideal behavior dominated by dipole-induced dipole interactions and structural accommodation of aniline molecules in the carbon tetrachloride matrix.

II.ii. Carbon Tetrachloride + Phenol (Nonpolar + Nonpolar) System

In this system, ultrasonic velocity increases progressively with mole fraction, demonstrating enhancement in interaction strength due to the presence of phenol molecules (Fig. 1; Table 2). Density decreases smoothly with increasing phenol concentration, which reflects reduction in effective packing efficiency due to size and structural differences between the components.

The decreasing trend in adiabatic compressibility indicates stronger cohesive interactions and increased structural rigidity with addition of phenol. Since phenol contains -OH group capable of hydrogen bonding, the observed behavior suggests partial association between phenol molecules along with weak interaction with nonpolar carbon tetrachloride through induced dipole forces.

The excess adiabatic compressibility values are positive throughout the composition range, implying weaker interactions between unlike molecules compared to self-associated phenol molecules. This indicates that addition of carbon tetrachloride disrupts the hydrogen-bonded structure of phenol, leading to loosening of the liquid structure.

Excess volume expansivity values are mostly negative, which indicates contraction in volume due to better accommodation of carbon tetrachloride molecules within phenol network. Thus, the system is characterized by dominance of dispersive and weak dipole-induced dipole interactions along with partial breaking of phenol hydrogen bonding network.

II.iii. Methanol + Acrolein (Polar + Polar) System

The polar-polar methanol-acrolein mixture exhibits distinctly different behavior compared to the previous nonpolar-polar systems. Ultrasonic velocity increases with mole fraction, indicating strengthening of intermolecular interactions and formation of associated complexes between methanol and acrolein molecules ((Fig. 1; Table 3). Density shows non-linear variation, suggesting structural rearrangement due to strong specific interactions. Methanol is a strongly hydrogen-bonded liquid, whereas acrolein contains a polar carbonyl group capable of accepting hydrogen bonds. Therefore, heteromolecular hydrogen bonding between -OH group of methanol and C=O group of acrolein is expected. Adiabatic compressibility initially decreases and then shows irregular variation at higher mole fractions, which indicates complex association and structural reorganization in the mixture. The excess adiabatic compressibility values are largely negative at lower mole fractions, confirming strong specific interactions and hydrogen bond formation between unlike molecules. However, positive deviation at higher mole fractions suggests weakening of heteromolecular association due to dominance of acrolein-acrolein interactions. The excess volume expansivity values remain negative throughout the composition range, revealing significant contraction in volume due to strong intermolecular attraction and compact structure formation. This clearly indicates strong specific interactions dominated by hydrogen bonding and dipole-dipole interactions in the polar-polar system.

III. EXPERIMENTAL

III.i. Materials

Carbon tetrachloride, aniline, phenol, methanol, and acrolein of analytical reagent (AR) grade purity (>99%) were procured from standard commercial suppliers and used without further purification. The purity of the chemicals was confirmed by comparing the experimentally measured densities with standard literature values.

Binary mixtures were prepared by mass using an electronic analytical balance with an accuracy of ± 0.0001 g. The mole fraction uncertainty was estimated to be within ± 0.0002 . Fresh mixtures were prepared prior to each measurement to avoid composition changes due to evaporation.

III.ii. Measurements

All measurements were carried out at a constant temperature of (298.15 ± 0.01) K, maintained using a thermostatically controlled water bath. The temperature stability was monitored using a calibrated digital thermometer.

Ultrasonic velocity (U) was measured using a single crystal ultrasonic interferometer operating at a fixed frequency of 2 MHz with an accuracy of $\pm 0.1\%$. The instrument was calibrated using standard liquids before measurements.

Density (ρ) measurements were performed using a 10 mL specific gravity bottle with an accuracy of ± 0.0001 g cm⁻³. The bottle was thoroughly cleaned and dried before each measurement.

Viscosity (η) was determined using an Ostwald viscometer with a flow time accuracy of ± 0.1 s. Each flow time was recorded as the average of three successive measurements.

All experimental measurements were repeated three times, and the average values were reported. The maximum estimated uncertainties were $\pm 0.1\%$ for ultrasonic velocity, ± 0.0001 g cm⁻³ for density, and $\pm 0.2\%$ for viscosity. The uncertainty in calculated adiabatic compressibility was estimated to be within $\pm 0.5\%$.

IV. Governing Equations

The following standard thermodynamic and acoustic relations were used to calculate the derived parameters from experimentally measured ultrasonic velocity, density, and viscosity data at 303.15 K.

IV. i. Adiabatic Compressibility (β)

$$\beta = 1 / (\rho U^2)$$

Where ρ is the density of the mixture and U is the ultrasonic velocity.

IV. ii. Intermolecular Free Length (Lf)

$$L_f = K_T \sqrt{\beta}; (K_T = 2.0112 \times 10^{-6})$$

Where K_T is the temperature-dependent Jacobson constant and β is the adiabatic compressibility.

IV. iii. Excess Property (Y^E)

$$Y^E = Y_{\text{mix}} - (x_1 Y_1 + x_2 Y_2)$$

Where Y represents any thermodynamic parameter such as β or α ; x_1 and x_2 are the mole fractions of components 1 and 2 respectively; Y_{mix} is the property of the mixture, and Y_1 and Y_2 are the properties of pure components.

IV. iv. Excess Viscosity (η^E)

$$\eta^E = \eta_{\text{mix}} - (x_1 \eta_1 + x_2 \eta_2)$$

Where η represents viscosity, and the symbols have their usual meaning.

Table 1. Carbon tetrachloride + Aniline (Non-polar + polar)

Mole fraction (Cm)	Ultra sonic velocity (μ) ms ⁻¹	Density (ρ) $\rho \times 10^3 \text{ kg m}^{-3}$	Adiabatic Compressibility (β) $\beta \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Volume expansivity (α) $\alpha \times 10^{-3} \text{ K}^{-1}$	Excess adiabatic Compressibility (β^E) $\beta^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Excess Volume expansivity (α^E) $\alpha^E \times 10^{-3} \text{ K}^{-1}$
0.0	903.22	1.5741	7.790	1.2377	---	---
0.1	949.10	1.5620	7.242	1.1181	-0.804	-0.05581
0.2	996.11	1.4771	6.625	1.1202	-2.288	0.01008
0.3	1049.75	1.4425	6.320	1.0165	-0.672	-0.02983
0.4	1100.20	1.3859	5.710	0.9517	-2.096	-0.03084
0.5	1180.41	1.3329	5.474	1.0123	0.220	0.0955
0.6	1240.62	1.2716	5.102	0.9520	1.176	0.09704
0.7	1322.70	1.2139	4.750	0.8075	2.332	0.01633
0.8	1407.10	1.2426	4.211	0.7200	1.618	-0.00738
0.9	1505.21	1.2510	3.550	0.6580	-0.316	-0.00559
1.0	1589.26	1.0625	3.114	0.5998	---	---

Table 2. Carbon tetrachloride + Phenol (Non-polar + Non-polar)

Mole fraction (Cm)	Ultra sonic velocity (μ) ms ⁻¹	Density (ρ) $\rho \times 10^3 \text{ kg m}^{-3}$	Adiabatic Compressibility (β) $\beta \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Volume expansivity (α) $\alpha \times 10^{-3} \text{ K}^{-1}$	Excess adiabatic Compressibility (β^E) $\beta^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Excess Volume expansivity (α^E) $\alpha^E \times 10^{-3} \text{ K}^{-1}$
0.0	903.22	1.5746	7.785	1.2319	---	---
0.1	930.10	1.5262	7.560	1.12567	0.1262	-0.05255
0.2	962.91	1.4817	7.280	1.0179	0.1974	-0.10664
0.3	1006.43	1.4362	6.874	1.04867	0.1426	-0.02219
0.4	1052.70	1.3864	6.510	1.0345	0.1298	-0.01732
0.5	1107.71	1.3413	6.075	0.9251	0.0460	-0.0384
0.6	1167.24	1.2895	5.690	0.9335	0.0122	-0.25436
0.7	1242.53	1.2304	5.263	0.7621	0.0636	-0.09404
0.8	1326.41	1.1753	4.836	0.7997	0.1394	-0.00276
0.9	1391.86	1.1262	4.585	0.7726	0.0392	-0.02382
1.0	1452.52	1.0648	4.273	0.6951	---	---

Table 3. Methanol + Acrolein (Polar + Polar)

Mole fraction (Cm)	Ultra sonic velocity (μ) ms ⁻¹	Density (ρ) $\rho \times 10^3 \text{ kg m}^{-3}$	Adiabatic Compressibility (β) $\beta \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Volume expansivity (α) $\alpha \times 10^{-3} \text{ K}^{-1}$	Excess adiabatic Compressibility (β^E) $\beta^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Excess Volume expansivity (α^E) $\alpha^E \times 10^{-3} \text{ K}^{-1}$
0.0	1086.15	0.7760	10.926	1.2777	---	---
0.1	1180.10	0.7824	9.180	1.2325	-1.0475	-0.24218
0.2	1232.00	0.7488	8.780	1.1506	-0.749	-0.52106
0.3	1275.10	0.7974	7.714	1.7232	-1.1165	-0.14544
0.4	1310.07	0.8157	7.144	1.7071	-0.988	-0.35852
0.5	1333.00	0.8172	6.946	1.8641	-0.4875	-0.3985
0.6	1350.01	0.8482	8.808	2.0081	2.1327	-0.5877
0.7	1360.04	0.9012	6.501	1.9920	0.4645	-0.66456
0.8	1365.10	0.8326	6.445	2.3982	1.107	-0.45534
0.9	1373.00	0.8401	6.311	2.4281	1.6716	-0.80242
1.0	1438.00	0.8061	3.941	3.2475	---	---

V. Conclusion

The variation of ultrasonic velocity, density, adiabatic compressibility, free length, excess compressibility, and excess free length with mole fraction reveals significant insights into intermolecular interactions in the studied binary liquid mixtures.

Ultrasonic velocity increases with mole fraction for all systems, indicating enhanced molecular association and stronger intermolecular interactions as the concentration of the second component increases. The density trends show a systematic variation, suggesting effective packing of molecules and changes in structural compactness of the mixtures.

Adiabatic compressibility decreases with increasing mole fraction, which signifies reduced compressibility of the medium and indicates stronger cohesive forces between unlike molecules. Correspondingly, the decrease in intermolecular free length supports closer molecular packing and stronger attractive interactions within the mixtures.

The excess compressibility and excess free length exhibit both positive and negative deviations depending on composition. Negative deviations at certain mole fractions indicate strong specific interactions such as dipole-dipole or hydrogen bonding between components, whereas positive deviations suggest weaker interactions or structural loosening in some composition ranges.

Overall, the combined analysis of acoustic and excess parameters confirms the presence of significant molecular interactions in the binary mixtures, with interaction strength varying systematically with mole fraction. These results demonstrate non-ideal behavior of the mixtures and highlight the dominance of specific intermolecular forces governing the thermodynamic and acoustic properties of the systems.

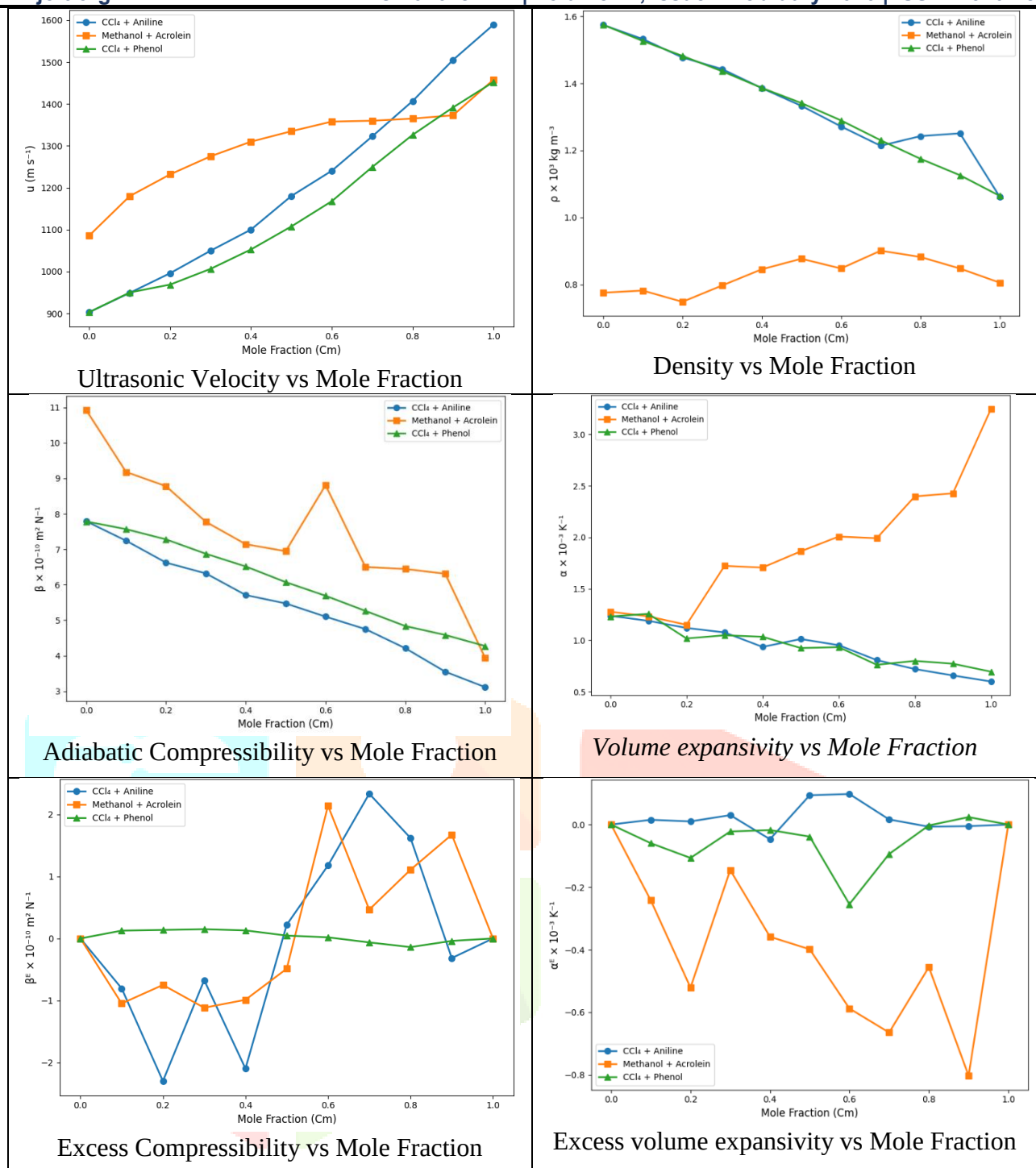


Fig 1. Mole Fraction Dependence of Acoustic and Thermodynamic Properties of Binary Liquid Systems

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