Study of Intermolecular Interactions in (Ethanol+ n- Heptanol + Acrylonitrile) Ternary Mixture Through Thermo-acoustic and Excess Parameters at Different Temperatures

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Abstract:
This research investigates the intermolecular interactions in the ternary liquid mixture of ethanol, n-heptanol, and acrylonitrile using thermo-acoustic parameters at 298.15, 303.15, and 308.15 K under atmospheric pressure. Ultrasonic velocity, viscosity, as well as density were experimentally measured over the entire composition range, and thermo-acoustic parameters like acoustic impedance, intermolecular free length, adiabatic compressibility, internal pressure, relaxation time, and free volume were evaluated using standard relations. The dip in ultrasonic density, velocity, along with acoustic impedance, together with the increase in intermolecular free length as well as adiabatic compressibility with rising ethanol concentration, indicates a gradual weakening of the self-associated hydrogen-bonded network of n-heptanol and reduced molecular packing. Rise in internal pressure and relaxation time proposes creation of heteromolecular associations through hydrogen bonding between the hydroxyl groups of ethanol and n-heptanol, along with dipole–dipole interactions involving the nitrile group of acrylonitrile. The observed variations demonstrate that the liquid structure is governed by the balance between the disruption of alcohol self-association and the formation of unlike molecular interactions. Increasing temperature weakens these interactions due to enhanced thermal agitation, resulting in reduced molecular association and structural ordering. The results confirm that thermo-acoustic parameters provide valuable insight in intermolecular interactions as well as structural behaviour of ethanol + n-heptanol + acrylonitrile ternary liquid system.

Key words: Ternary liquid mixture, Thermo-acoustic parameters, Intermolecular interactions, Ultrasonic velocity, Hydrogen bonding, Acrylonitrile

1. Introduction

Assessment of molecular interactions in liquid mixtures is significantly important in physical chemistry, as these interactions dictate the thermodynamic, acoustic, and transport aspects of multicomponent systems. Thermo-acoustic investigations, and assessment of surplus parameters, offer a dependable method for understanding characteristics as well as intensity of intermolecular forces between dissimilar molecules. [1] Such investigations are essential for elucidating the structural configuration of molecules and their divergence from perfect mixing behaviour.

The ternary liquid system including ethanol, n-heptanol, and acrylonitrile has been chosen for its unique physicochemical properties. Ethanol is a polar protic solvent with a hydroxyl group that can generate robust intermolecular hydrogen bonds. n-Heptanol, a higher aliphatic alcohol, possesses a hydroxyl group and features an extended hydrophobic hydrocarbon chain, resulting in a balance between hydrogen bonding and dispersion forces. Acrylonitrile is a polar aprotic molecule featuring a strongly electronegative nitrile (–C≡N) group, which engenders substantial dipole–dipole interactions but does not engage in hydrogen-bond donation.[2] The amalgamation of these three liquids leads to a sophisticated network of molecular interactions characterized by dipole-dipole attraction, hydrogen bonding, and dispersive forces.

The assessment of ultrasonic viscosity, density, as well as velocity across varying temperatures yields essential experimental data necessary for the computation of diverse thermo-acoustic parameters, including acoustic impedance, intermolecular free length, adiabatic compressibility, internal pressure, free volume, and relaxation time. [3] These characteristics are extremely responsive to alterations in molecular aggregation and structural arrangement within liquid mixture. Moreover, the assessment of excess properties—such as excess intermolecular free length, excess adiabatic compressibility, excess internal pressure, excess free volume, excess relaxation time, excess acoustic impedance, excess molar volume, excess viscosity, and deviation in ultrasonic velocity—provides significant insights into deviations from ideality and the characteristics of interactions between dissimilar molecules.

Temperature significantly influences molecule interactions by altering the degree of hydrogen bonding and molecular packing. An elevation in temperature typically diminishes intermolecular forces due to increased molecular mobility, leading to noticeable alterations in thermo-acoustic and excess characteristics. Consequently, measurements conducted at 298.15 K, 303.15 K, and 308.15 K elucidate the temperature dependency of molecule interaction within the ternary system.

2. Materials and Methods

2.1 Materials

Analytical reagent (AR) grade ethanol, n-heptanol, and acrylonitrile with purity greater than 99% were used for the present

investigation. The chemicals were procured from reputed commercial suppliers and utilized without additional purification. Before use, the liquids were stored in airtight containers to minimize contamination and moisture absorption. [4] Purity of the samples was verified by comparing experimentally measured densities and ultrasonic velocities of the pure components with the reported literature values at the corresponding temperatures.

\2.2 Preparation of Ternary Mixtures

The ternary mixtures of ethanol (x_1), n-heptanol (x_2), and acrylonitrile (x_3) were prepared gravimetrically using a digital analytical balance with an precision of ±0.0001 g. Mole fraction of n-heptanol was maintained constant ($x_2 = 0.30$), while the mole fraction of ethanol was varied from 0.00 to 0.70, with the corresponding mole fraction of acrylonitrile adjusted to satisfy the relation $x_1 + x_2 + x_3 = 1$. The prepared mixtures were thoroughly mixed then permitted to attain equilibrium before measurements. [5]

2.3 Experimental Measurements

Ultrasonic velocity of mixtures was measured utilizing a single-crystal ultrasonic interferometer operating at a fix frequency of 2 MHz. Density measurements were carried out using a calibrated 25 mL specific gravity bottle (pycnometer), while viscosity was determined using a calibrated Ostwald viscometer. [6] All measurements were performed at 298.15, 303.15, and 308.15 K under atmospheric pressure. A thermostatically controlled circulating water bath with a temperature stability of ±0.1 K was utilized to maintain the desired experimental temperature throughout the measurements. All measurements were repeated at least three times, and mean values were utilized for subsequent calculations.

2.4 Evaluation of Thermo-acoustic Parameters

Experimentally measured values of viscosity (η), density (ρ), and ultrasonic velocity (U) were utilized to evaluate the thermo-acoustic parameters employing standard theoretical relations. The calculated parameters include intermolecular free length (Lf), adiabatic compressibility (β), internal pressure (πi), acoustic impedance (Z), free volume (Vf), and relaxation time (τ). These parameters provide valuable information regarding molecular packing, compressibility, and nature of intermolecular interactions in the ternary liquid system. [7] The variations of these parameters with composition and temperature were analysed to comprehend structural behaviour and molecular association in the ethanol + n-heptanol + acrylonitrile mixture.

2. Results

A thermo-acoustic study of the ternary liquid system including ethanol, n-heptanol, and acrylonitrile was conducted by experimentally measuring viscosity, density, as well as ultrasonic velocity at 298.15 K, 303.15 K, and 308.15 K across the complete composition spectrum. [8] These essential features form the foundation for assessing molecular behaviour and intermolecular interactions within the mixture. Experimental data were utilized to determine several thermo-acoustic characteristics, involving intermolecular free length, adiabatic compressibility, internal pressure, free volume, relaxation time, acoustic impedance, and molar volume. The fluctuation of both actual and estimated parameters with respect to mole fraction and temperature yields significant insights into molecular association, structural configuration, and deviations from ideal behaviour. The experimental and calculated results are displayed in the following tables and analysed comprehensively in the succeeding sections. [9]

Table 1: Experimental Values of Viscosity (η), Density (ρ) and Ultrasonic Velocity (U) for the Ternary System (Ethanol + n-Heptanol + Acrylonitrile) at 298.15 K, 303.15 K, and 308.15 K

Mole Fraction			Viscosity(η) (10^{-3}Ns·m^{-2})			Density (ρ) Kg/m^3			Ultrasonic velocity (U) m·s^{-1}		
X1	X2	X3	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0	0.3	0.7	2.025	1.86	1.67	812.3	810.5	805.9	1234	1225	1219
0.1	0.3	0.6	2.068	1.93	1.817	809.7	807.8	803.2	1228	1221	1216
0.2	0.3	0.5	2.19	1.986	1.86	806.9	805.2	799.8	1223	1218	1212
0.3	0.3	0.4	2.27	2.03	1.896	805.2	803.5	796.9	1220	1216	1205
0.4	0.3	0.3	2.34	2.058	1.915	801.9	799.8	793.5	1217	1212	1199
0.5	0.3	0.2	2.38	2.17	1.935	799.3	795.2	791.6	1215	1209	1193
0.6	0.3	0.1	2.43	2.25	1.964	796.2	791.5	788.9	1210	1205	1189
0.7	0.3	0	2.51	2.354	2.054	791.4	787.8	785.2	1206	1201	1185

Table 2: Calculated Values of Free Volume (Vf), Free Length (Lf), and Adiabatic Compressibility (β) for the Ternary System (Ethanol + n-Heptanol + Acrylonitrile) at 298.15 K, 303.15 K, and 308.15 K

Mole Fraction			**Adiabatic Compressibility (β) (10^{-10}) Pa^{-1}**			**Free Length (Lf) (10^{-11}) m**			**Free Volume (Vf) (10^{-6}) m^3mol^{-1}**		
X1	X2	X3	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0	0.3	0.7	8.08	8.22	8.35	5.82	5.87	5.92	1.32	1.21	1.08
0.1	0.3	0.6	8.18	8.30	8.41	5.86	5.90	5.94	1.33	1.24	1.16
0.2	0.3	0.5	8.28	8.37	8.51	5.90	5.93	5.98	1.39	1.26	1.17
0.3	0.3	0.4	8.34	8.41	8.64	5.92	5.94	6.02	1.43	1.27	1.17
0.4	0.3	0.3	8.41	8.51	8.76	5.94	5.98	6.06	1.45	1.27	1.17
0.5	0.3	0.2	8.47	8.60	8.87	5.96	6.05	6.10	1.46	1.32	1.16
0.6	0.3	0.1	8.57	8.70	8.96	6.00	6.09	6.13	1.47	1.35	1.16
0.7	0.3	0	8.68	8.80	9.06	6.04	6.08	6.17	1.50	1.40	1.20

Table 3: Calculated Values of Internal Pressure (πi), Acoustic Impedance (Z) and Relaxation Time (τ) for the Ternary System (Ethanol + n-Heptanol + Acrylonitrile) at 298.15 K, 303.15 K, and 308.15 K

Mole Fraction			**Internal Pressure (πi) (10^8) Pa**			**Acoustic Impedance (Z) (106) kg/m^2s**			**Relaxation Time (τ) (10^{-12}) s**		
X1	X2	X3	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0	0.3	0.7	7.74	7.56	7.27	1.00	0.99	0.98	2.18	2.03	1.85
0.1	0.3	0.6	7.92	7.79	7.67	0.99	0.98	0.97	2.25	2.13	2.03
0.2	0.3	0.5	8.24	7.98	7.84	0.98	0.98	0.96	2.41	2.21	2.11
0.3	0.3	0.4	8.49	8.16	8.01	0.98	0.97	0.96	2.52	2.27	2.18
0.4	0.3	0.3	8.70	8.30	8.14	0.97	0.96	0.95	2.62	2.33	2.23
0.5	0.3	0.2	8.87	8.49	8.29	0.97	0.96	0.94	2.68	2.45	2.28
0.6	0.3	0.1	9.07	8.73	8.45	0.96	0.95	0.93	2.77	2.64	2.34
0.7	0.3	0	9.31	9.15	8.73	0.95	0.94	0.93	2.90	2.76	2.48

3. Discussion

The measured viscosity, density, and ultrasonic velocity data were used to evaluate the thermo-acoustic parameters of the ethanol + n-heptanol + acrylonitrile ternary system at diverse temperatures. [10] Variation of these parameters with composition provides valuable information regarding the strength as well as nature of intermolecular interactions in liquid mixture. Changes in molecular packing, hydrogen bonding, plus dipole–dipole interactions are reflected through the observed thermo-acoustic behaviour. Temperature also performs a crucial function in modifying these interactions by influencing molecular association and structural ordering. The calculated parameters are discussed regarding the molecular interactions governing ternary system and their dependence on composition and temperature. [11]

4.1 Ultrasonic Velocity: The ultrasonic velocity decreases continuously with increasing ethanol mole fraction at 298.15, 303.15, and 308.15 K, with the highest values observed at 298.15 K. This trend indicates weakening cohesive forces and molecular association due to the gradual disruption of the hydrogen-bonded network of n-heptanol. The newly formed ethanol–acrylonitrile interactions are comparatively weaker, resulting in a less rigid liquid structure and slower ultrasonic wave propagation. [12] The further decrease with temperature confirms that thermal agitation weakens intermolecular interactions.

4.2 Density: The density decreases with increasing ethanol concentration at all temperatures, indicating reduced molecular packing efficiency. Since ethanol has lower density than n-heptanol and acrylonitrile, its addition lowers the

overall density of the mixture. The disruption of hydrogen-bonded aggregates and thermal expansion at higher temperatures further reduce density by increasing intermolecular spacing. [13]

4.3 Viscosity: The viscosity of the ethanol + n-heptanol + acrylonitrile ternary mixture increases progressively with rising ethanol mole fraction at all temperatures, indicating enhanced intermolecular interactions. This behaviour suggests formation of heteromolecular hydrogen bonding between the hydroxyl groups of ethanol along with n-heptanol, together with dipole–dipole interactions involving the nitrile group of acrylonitrile, which restrict molecular mobility. The viscosity decreases with increasing temperature (298.15 K > 303.15 K > 308.15 K) due to thermal agitation that weakens intermolecular attractive forces and facilitates molecular motion. [14] Overall, the observed trend confirms that attractive molecular interactions govern the structural behaviour of the ternary liquid mixture.

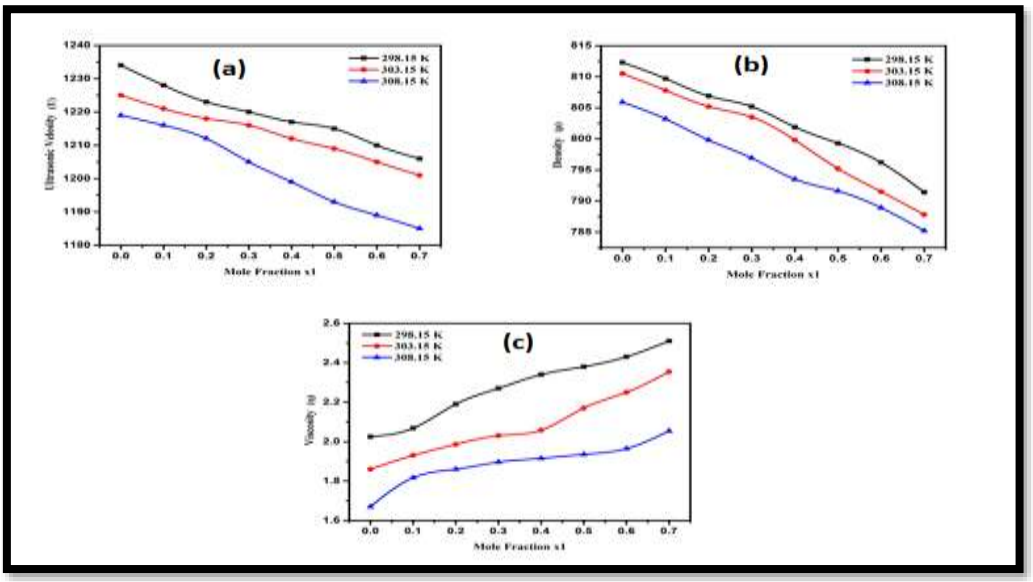

Fig. 1 Variation of Ultrasonic Velocity, Density and Viscosity with Mole Fraction (X_1) for the (Ethanol + n-Heptanol + Acrylonitrile) Ternary System at 298.15 K, 303.15 K, and 308.15 K

4.4 Adiabatic Compressibility: Adiabatic compressibility increases with ethanol concentration and temperature, indicating weaker intermolecular cohesion. The breakdown of the hydrogen-bonded n-heptanol network and its partial replacement by weaker ethanol–acrylonitrile interactions make the liquid structure more compressible. Elevated temperature further weakens molecular attractions. [15]

4.5 Intermolecular Free Length: Intermolecular free length increases with ethanol mole fraction and temperature, reflecting increased average molecular separation. This behaviour results from the disruption of hydrogen-bonded clusters and enhanced thermal motion, leading to a less compact and more disordered liquid structure. [16]

4.6 Free Volume: It raises with increasing ethanol mole fraction at all temperatures, indicating reduced molecular packing and greater intermolecular space owing to disruption of the self-associated hydrogen-bonded network of n-heptanol. Formation of ethanol–acrylonitrile hydrogen bonding and dipole–dipole interactions cannot completely compensate for this structural loosening, resulting in a more open liquid structure. [17] Dip in free volume with increasing temperature (298.15 K > 303.15 K > 308.15 K) reflects the enhanced molecular mobility and weakening of intermolecular attractive forces caused by thermal agitation.

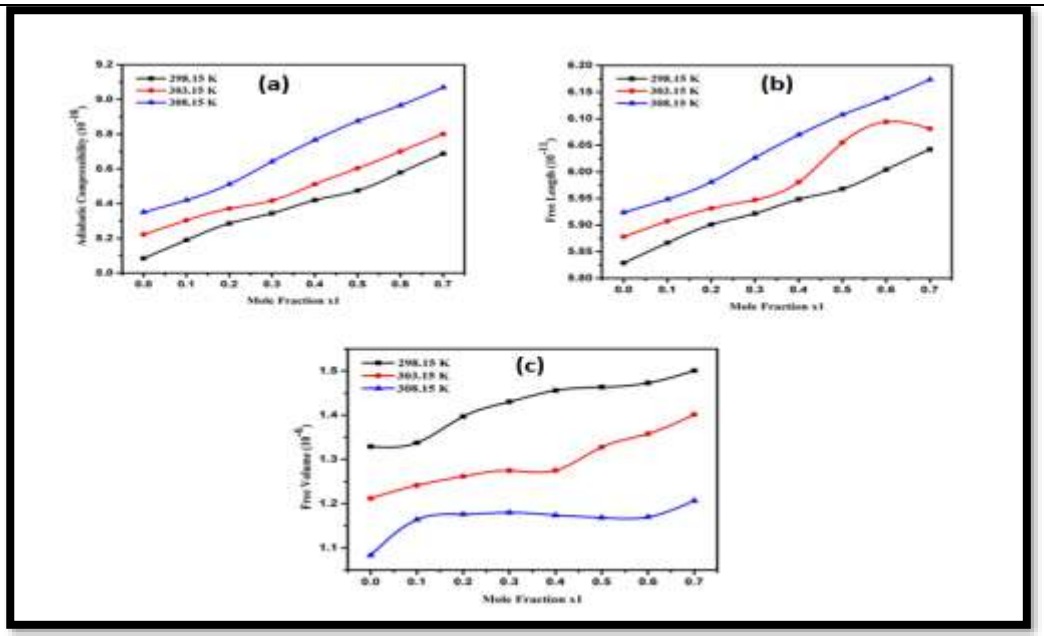

Fig. 2 Variation of Adiabatic Compressibility, Free Length and Free Volume with Mole Fraction (X_1) for the (Ethanol + n-Heptanol + Acrylonitrile) Ternary System at 298.15 K, 303.15 K, and 308.15 K

4.7 Internal Pressure: Internal pressure increases with ethanol concentration but decreases with temperature. The increase suggests formation of heteromolecular interactions by hydrogen bonding amid ethanol and n-heptanol and dipole–dipole interactions with acrylonitrile. [18] Higher temperatures weaken these cohesive interactions because of increased molecular mobility.

4.8 Acoustic Impedance: Acoustic impedance decreases steadily with increasing ethanol concentration and temperature due to the simultaneous reduction in ultrasonic velocity and density. [19] This indicates weaker cohesive forces, lower molecular packing, and reduced resistance to ultrasonic wave propagation.

4.9 Relaxation Time: Relaxation time increases with ethanol concentration and decreases with temperature. The increase reflects the formation of associated molecular complexes that delay molecular rearrangement after ultrasonic disturbance. [20] At higher temperatures, enhanced molecular motion accelerates relaxation, resulting in shorter relaxation times.

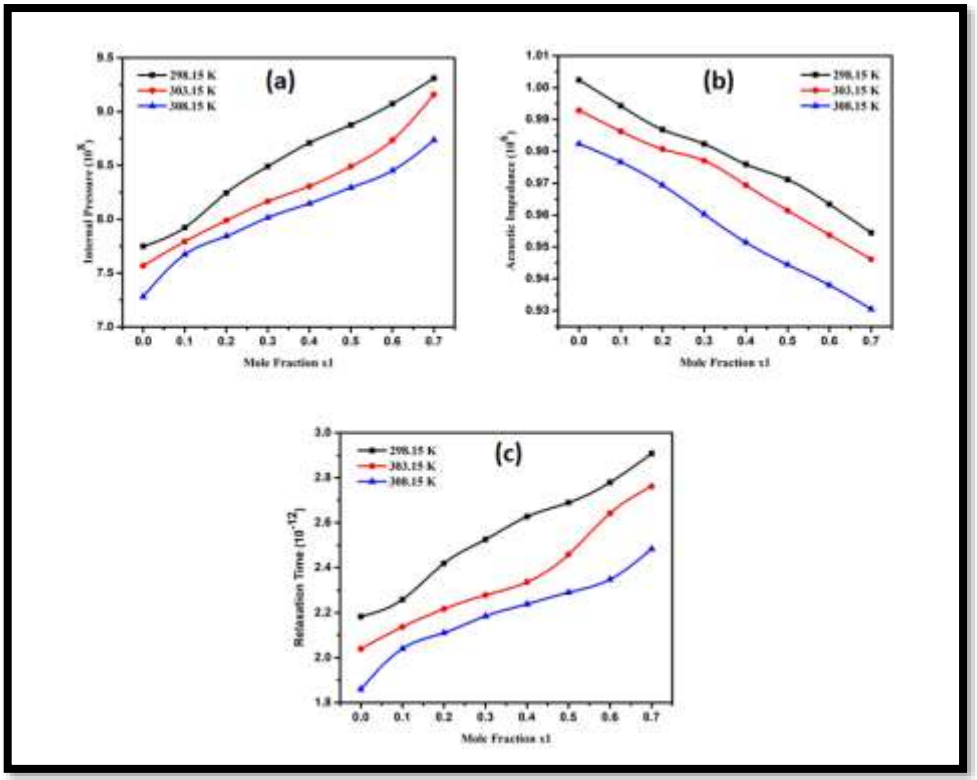

Fig. 3 Variation of Internal Pressure, Acoustic Impedance and Relaxation Time with Mole Fraction (X_1) for the (Ethanol + n-Heptanol + Acrylonitrile) Ternary System at 298.15 K, 303.15 K, and 308.15 K

5. Results:

The thermo-acoustic properties of ethanol + n-heptanol + acrylonitrile ternary mixture were investigated at 308.15, 303.15, and 298.15 K over the selected composition range. The experimental results showed that ultrasonic velocity, density, and acoustic impedance decreased with increasing ethanol mole fraction, whereas adiabatic compressibility, intermolecular free length, internal pressure, and relaxation time increased. These trends indicate significant changes in molecular packing and intermolecular interactions with composition. The observed variations suggest the gradual disruption of the hydrogen-bonded network of n-heptanol and the formation of new heteromolecular associations involving ethanol and acrylonitrile. Increasing temperature caused a reduction in ultrasonic velocity, density, acoustic impedance, internal pressure, and relaxation time, while adiabatic compressibility and intermolecular free length increased. This behaviour reflects the weakening of cohesive forces due to thermal agitation. Overall, the experimental findings demonstrate that the thermo-acoustic parameters are highly sensitive to composition and temperature and provide valuable insight into the structural organization and intermolecular interactions in the ethanol + n-heptanol + acrylonitrile ternary liquid system.

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