RESEARCH ARTICLE

ULTRASONIC–THERMO PHYSICAL INVESTIGATION OF TEMPERATURE-DEPENDENT MOLECULAR INTERACTIONS IN NON-IDEAL BINARY LIQUID MIXTURES

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Abstract:

The present study investigates the thermodynamic and acoustic behavior of binary liquid mixtures of 1-Butanol and Dodecane over a wide range of compositions and temperatures (288.15 K to 318.15 K). A comprehensive analysis was performed to determine critical parameters including thermal expansion coefficient (α), ultrasonic speed (U), acoustic impedance (Z), internal pressure (P_i), specific heat capacities at constant pressure (C_P) and volume (C_V), and the heat capacity ratio (ϒ). The pseudo-Gruneisen parameter (Γ) was also evaluated to gain insight into an-harmonic molecular behavior. The results reveal a systematic variation of these properties with both composition and temperature, indicating strong molecular interactions, particularly hydrogen bonding, within the mixture. A decrease in isothermal and isentropic compressibility with increasing mole fraction of 1-Butanol suggests denser molecular packing and reduced free volume. The decline in ultrasonic speed and acoustic impedance with temperature reflects thermal expansion and weakening of cohesive forces. Internal pressure analysis further confirms the influence of specific molecular interactions and structural rearrangements. Changes in heat capacities and the heat capacity ratio demonstrate the evolving energy storage capacity of the mixture under thermal stress. The increasing trend in pseudo-Gruneisen parameters points toward enhanced Vibrational anharmonicity at higher 1-Butanol concentrations.

Keyword: Thermal Expansion Coefficient, Ultrasonic Speed, Internal Pressure, Heat Capacity Ratio, Pseudo-Gruneisen Parameters, Butanol.

Introduction:

The study of liquid mixtures offers valuable insights into molecular interactions, salvation phenomena, and energy transfer mechanisms. When two or more liquids are combined, their individual molecular characteristics interact, often producing non-ideal behaviours that reveal important information about intermolecular forces such as hydrogen bonding, van der Waals interactions, and dipole–dipole attractions. These interactions affect critical thermo physical properties, including compressibility, thermal expansion, heat capacity, and sound velocity, which are essential for understanding and predicting mixture behavior.The present investigation deals with 1-Butanol and Dodecane liquids that have various industrial and pharmaceutical applications. 1-Butanol is commonly used as a solvent[1] for resins, dyes, alkaloids, plasticizer[2] component due to its ability to dissolve both polar and non-polar substances. It is particularly useful in the production of pharmaceuticals and synthetic intermediates[3]. It is an alternative source of biofuel[4] due to low volatility and higher energy content than ethyl alcohol whereas Dodecane is heat transfer[5] and cooling fluid that acts as a carrier or dispersing medium for controlling particle growth and stability in hydrophobic environments. In the continuation of previously published work[6-10], this paper is concerned with the theoretical investigation of various thermodynamic and acoustical properties from the knowledge of thermal expansion coefficient, isothermal compressibility and isentropic compressibility by statistical model of Flory[11-12] over the entire range of mole fraction at different temperature and atmospheric pressure and compared with the literature[13]. The derivative of internal energy with respect to volume under constant temperature, expressed as $(\partial E/\partial V)_T$ defines the internal pressure. An attempt was made to estimate internal pressure indirectly through the methodology suggested by Suryanarayan[14]. More over pseudo-gruneisen parameter (Γ) was also evaluated to analyze an-harmonic molecular behavior. The main purpose of the work was to investigate molecular interactions, structural rearrangements and Vibrational anharmonicity at different concentrations.

Theoretical Formulation:

In this investigation following relations were used to analyze investigate molecular interactions, structural and an-harmonic behavior at different temperatures and varying concentrations.

$$U = \left(\frac{\sigma}{6.3 \times 10^{-4}\rho_{Mix}}\right)^{2/3} \quad (1)$$

$$Z = (U) \times (\rho_{Mix}) \quad (2)$$

$$\beta_S = \left[\frac{1}{u^2\rho_{Mix}}\right] \quad (3)$$

$$P_{i,Flory} = T \cdot \gamma_P \quad (4)$$

$$\Gamma_{Flory} = \frac{U^2\alpha}{C_P} \qquad (5)$$

$$C_{P,Mix} = C_P^E + C_P^{Idel} \qquad (6)$$

$$C_P^{Ideal} = \sum_{i=1}^{2} x_i C_{P,i} \qquad (7)$$

$$C_P^E = \frac{P^*V^*}{T^*}\left[\frac{1}{\left(\left(4/3\right)\tilde{V}_i^{-1/3} - 1\right)} - \sum\left\{\frac{x_i}{\left(\left(4/3\right)\tilde{V}_i^{-1/3} - 1\right)}\right\}\right] \qquad (8)$$

Result and Discussion:

The thermodynamic and transport properties of the binary system comprising 1-Butanol and Dodecane were investigated over a range of mole fractions at four different temperatures: 288.15 K, 298.15 K, 308.15 K, and 318.15 K. The study focused on parameters such as the thermal expansion coefficient (α), isothermal compressibility (β_T), isentropic compressibility (β_S), ultrasonic velocity (U), acoustic impedance (Z), internal pressure (P_i) specific heat capacities (C_P and C_V), the heat capacity ratio (ϒ), and the pseudo gruneisen parameter (Γ) are presented in table1 .At each temperature, the thermal expansion coefficient α showed a slight decrease with increasing mole fraction of 1-Butanol. This trend was consistent across the temperature range, suggesting that molecular expansion became slightly restricted as more polar molecules were introduced into the system. Isothermal and isentropic compressibility's also declined with increasing mole fraction, indicating reduced free volume and enhanced intermolecular interactions.

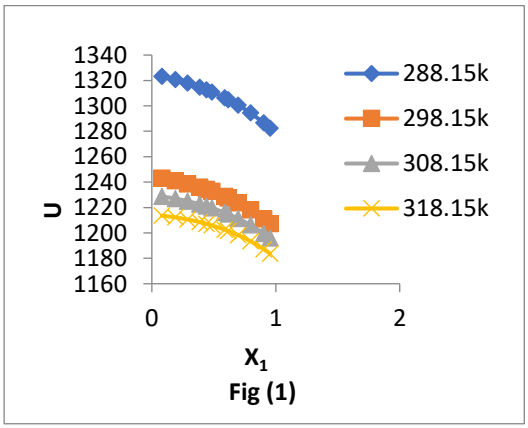

Fig (1)

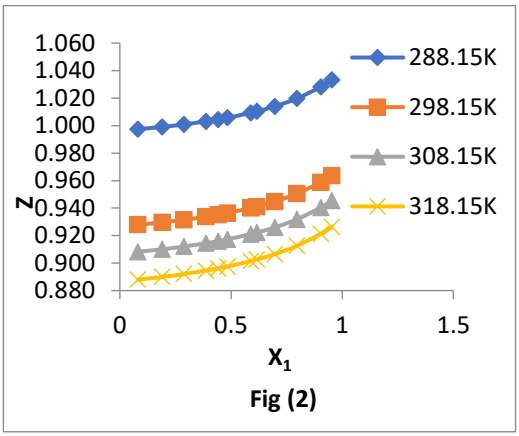

Fig (2)

The presence of hydrogen bonding in 1-Butanol likely contributed to this observation, as such interactions lead to a more compact and less compressible system. Additionally, the decrease in compressibility was more pronounced at higher temperatures, which is typical of systems where molecular motion increases but cohesive interactions are still significant. A very close observation of table 1 reveals that isentropic compressibility (β_S) suggests that at lower temperatures 288.15 K**,** molecules are more tightly packed due to reduced kinetic energy, resulting in lower compressibility whereas **at** higher temperatures 318.15 K**,** increased molecular motion leads to looser molecular packing, greater intermolecular distances, and therefore higher compressibility. Ultrasonic velocity (U)

exhibited a gradual decrease with both mole fraction and temperature. This behavior can be attributed to the increase in molecular disorder and the reduction in cohesive forces in the mixture as 1-Butanol content increases as shown in figure1.The highest values of U are recorded at 288.15 K, with values declining progressively at higher temperatures. This is consistent with the thermal weakening of molecular forces and increased compressibility at elevated temperatures. Correspondingly, acoustic impedance (Z), which depends on both density and velocity, also decreased with temperature. It exhibits a non-linear increase with mole fraction of 1-Butanol as shown in figure 2. The rise in Z is more prominent at lower temperatures, particularly at 288.15 K, where molecular packing and cohesive interactions are strongest but as the temperature increases, the impedance decreases across all compositions due to diminished intermolecular attraction and lower densities. This behavior confirms the combined effects of polarity and molecular mass on sound propagation resistance in the mixture. However, its variation with composition was relatively small; reflecting minimal changes in density over the composition range. Internal pressure (P_i) shows a non-linear increase with increasing mole fraction of 1-Butanol (X_1) at all temperatures as shown in figure 3. The highest values of P_i are observed at lower temperatures (288.15 K), and the lowest at 318.15 K, for corresponding compositions. The rise in internal pressure with increasing 1-Butanol concentration can be attributed to the presence of strong polar interactions, particularly hydrogen bonding between hydroxyl groups of 1-Butanol molecules. As the composition shifts from non-polar Dodecane toward polar 1-Butanol, the cohesive energy density of the system increases due to these directional forces, leading to higher internal pressure values. Temperature has a clear inverse effect on internal pressure. The specific heat capacities C_P and C_V followed a decreasing trend with increasing 1-Butanol content and rising temperature.

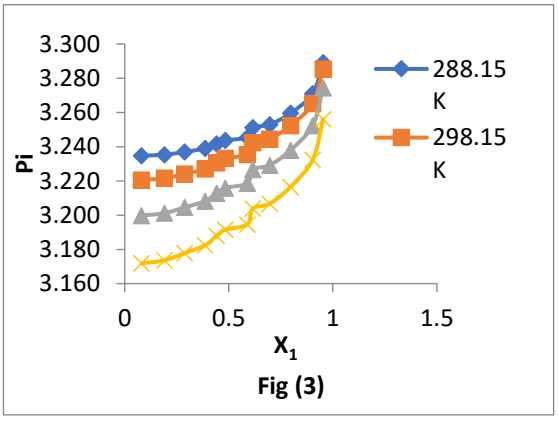

Fig (3)

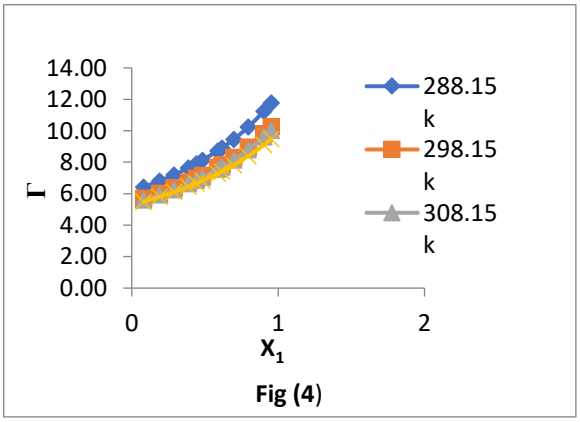

Fig (4)

This behavior implies a reduction in the system's ability to store energy as Vibrational or translational motion, possibly due to a more ordered molecular arrangement induced by hydrogen bonding. Despite this, the heat capacity ratio ($\Upsilon = C_P//C_V$) remained nearly constant, showing only a slight decrease from around 1.53 at 288.15 K to about 1.45 at 318.15 K. This constancy indicates that the relative distribution of energy storage under constant pressure and constant volume does not change significantly across the studied conditions. The pseudo gruneisen parameter (Γ), which reflects anharmonicity in molecular vibrations and interactions, increased with mole fraction and temperature. This suggests that the mixture becomes more anharmonic with the addition of 1-Butanol, especially at higher thermal energies. The increase in τ aligns with the expectation of enhanced molecular disorder and thermal expansion effects in more polar-rich mixtures.

X_1	α X10^3	β_T x10^{12}	U	βs x10^{12}	Z x 10^{-6}	C_p	P_i	C_V	Γ	Υ
				T=288.15K						
0.08048	1.303	116.065	1323.13	757.75	0.997	355.20	3.235	231.88	6.42	1.53
0.19017	1.301	115.852	1320.62	757.94	0.999	333.15	3.235	217.90	6.81	1.53
0.28812	1.300	115.642	1317.85	758.16	1.001	313.46	3.237	205.45	7.20	1.53
0.38654	1.298	115.406	1314.64	758.36	1.003	293.67	3.239	192.93	7.64	1.52
0.44097	1.297	115.260	1312.62	758.46	1.004	282.73	3.242	186.02	7.91	1.52
0.4835	1.297	115.137	1310.94	758.51	1.006	274.18	3.244	180.61	8.13	1.52
0.58849	1.295	114.789	1306.21	758.56	1.009	253.07	3.245	167.23	8.73	1.51
0.61515	1.295	114.688	1304.86	758.54	1.010	247.71	3.251	163.84	8.90	1.51
0.69605	1.293	114.342	1300.56	758.32	1.014	231.45	3.253	153.54	9.45	1.51
0.79594	1.292	113.804	1294.43	757.61	1.020	211.37	3.260	140.84	10.24	1.50
0.90295	1.290	113.026	1286.55	756.02	1.028	189.85	3.271	127.26	11.25	1.49
0.95321	1.289	112.556	1282.34	754.78	1.033	179.93	3.289	120.86	11.78	1.49
				T=298.15K						
0.08048	1.329	123.067	1242.96	867.06	0.928	359.94	3.221	253.91	5.70	1.42
0.19017	1.328	122.935	1240.95	866.84	0.930	338.09	3.222	239.01	6.04	1.41
0.28812	1.326	122.648	1238.65	866.69	0.932	318.58	3.224	225.68	6.38	1.41
0.38654	1.324	122.369	1235.94	866.50	0.934	298.98	3.227	212.29	6.76	1.41
0.44097	1.323	122.058	1234.22	866.36	0.935	288.14	3.231	204.87	6.99	1.41
0.4835	1.322	121.869	1232.78	866.23	0.936	279.67	3.233	199.07	7.18	1.40
0.58849	1.321	121.711	1228.68	865.78	0.940	258.76	3.235	184.83	7.69	1.40
0.61515	1.319	121.270	1227.48	865.64	0.941	253.45	3.242	181.13	7.84	1.40
0.69605	1.318	121.144	1223.72	864.96	0.945	237.33	3.245	170.19	8.31	1.39
0.79594	1.317	120.716	1218.25	863.62	0.950	217.44	3.252	156.64	8.98	1.39
0.90295	1.315	120.066	1211.19	861.17	0.959	196.12	3.265	142.16	9.82	1.38
0.95321	1.313	119.146	1207.41	859.43	0.964	186.29	3.285	135.27	10.27	1.38
				T=308.15K						

0.08048	1.355	130.401	1228.72	896.14	0.908	364.79	3.200	250.79	5.61	1.45
0.19017	1.352	130.035	1227.03	895.53	0.910	342.80	3.201	236.24	5.94	1.45
0.28812	1.350	129.681	1225.05	895.00	0.912	323.17	3.205	223.17	6.27	1.45
0.38654	1.348	129.291	1222.63	894.43	0.914	303.44	3.208	210.06	6.64	1.44
0.44097	1.347	129.055	1221.09	894.08	0.916	292.53	3.213	202.74	6.86	1.44
0.4835	1.346	128.859	1219.77	893.77	0.917	284.01	3.216	197.06	7.05	1.44
0.58849	1.344	128.319	1216.04	892.86	0.921	262.96	3.219	183.16	7.56	1.44
0.61515	1.343	128.166	1214.91	892.60	0.922	257.62	3.227	179.47	7.69	1.44
0.69605	1.341	127.652	1211.39	891.53	0.926	241.40	3.229	168.80	8.15	1.43
0.79594	1.339	126.882	1206.25	889.67	0.932	221.38	3.238	155.55	8.80	1.42
0.90295	1.337	125.811	1199.55	886.58	0.940	199.93	3.252	141.38	9.62	1.41
0.95321	1.336	125.184	1195.93	884.50	0.945	190.03	3.274	134.58	10.05	1.41
				T=318.15K						
0.08048	1.382	138.576	1213.61	927.98	0.888	370.66	3.172	248.37	5.49	1.49
0.19017	1.380	138.119	1212.25	926.94	0.890	349.33	3.174	234.71	5.80	1.49
0.28812	1.377	137.680	1210.60	926.00	0.892	330.28	3.178	222.37	6.11	1.49
0.38654	1.375	137.199	1208.52	925.00	0.895	311.15	3.182	210.00	6.45	1.48
0.44097	1.373	136.911	1207.15	924.41	0.896	300.56	3.188	203.07	6.66	1.48
0.4835	1.372	136.673	1205.95	923.92	0.898	292.29	3.191	197.70	6.83	1.48
0.58849	1.370	136.020	1202.61	922.48	0.901	271.88	3.195	184.67	7.29	1.47
0.61515	1.369	135.837	1201.54	922.10	0.903	266.70	3.204	181.12	7.41	1.47
0.69605	1.367	135.225	1198.32	920.60	0.906	250.97	3.207	171.13	7.82	1.47
0.79594	1.365	134.319	1193.51	918.17	0.913	231.54	3.216	158.70	8.40	1.46
0.90295	1.362	133.080	1187.16	914.38	0.921	210.74	3.232	145.40	9.11	1.45
0.95321	1.361	132.362	1183.71	911.94	0.926	201.14	3.256	138.95	9.48	1.45

Conclusion:

The comparative evaluation of thermodynamic and acoustic parameters for the 1-Butanol + Dodecane binary mixture across the temperature range of 288.15–318.15 K reveals a clear interplay between temperature, composition, and molecular interactions. At lower temperatures, the system exhibits pronounced structural rigidity, reflected in elevated ultrasonic velocity, internal pressure, and acoustic impedance, along with a marked reduction in isentropic compressibility. These characteristics indicate dominant hydrogen-bonding interactions among 1-Butanol molecules and effective molecular packing in the mixture. As the temperature rises, a gradual decline in these cohesive forces is observed, accompanied by increased molecular flexibility and compressibility, signifying the disruption of hydrogen-bond networks and a shift towards a more disordered molecular arrangement. The uniform trends among all parameters confirm the non-ideal mixing nature of the system, where both polar–polar and polar–non-polar interactions govern its behavior.

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