Molecular Interaction in Binary Mixtures of Benzyl propionate with methanol at different temperatures: An Ultrasonic study

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Abstract:

At temperatures 308 K, 313 K, 318 K, 323 K, 328 K, and 333 K, the density (ρ), speed of sound (u), and viscosity (η) of binary liquid solutions containing benzyl propionate with methanol were determined over the full range of composition. Various thermo-acoustical characteristics have been done to analyze the intermolecular interactions between the molecules of liquid mixtures. By the calculated parameters likeacoustic impedance (Z), adiabatic compressibility (β_a), Intermolecular free length (L_f), relaxation time (τ), and internal pressure (π) It has been confirmed that liquid mixture components exhibit strong hetero association.Other thermodynamic parameters like Gibb's free energy (ΔG) and enthalpy (H) have also been calculated. The linear variations are found for the thermo-acoustic parameters which imply the presence of solute-solvent interactions in the binary system that strengthens the above findings.

Keywords: benzyl propionate,methanol, acoustic impedance, adiabatic compressibility, Intermolecular free length, relaxation time, internal pressure

DOINumber:10.48047/nq.2022.20.22.NQ10366 **NeuroQuantology2022;20(22):3674-3682**

Introduction:

When analyzing the physico-chemical behaviour of liquid mixtures and the intensity of the molecular connection between the solute and solvent, ultrasonic research is quite helpful[1,2]. All disciplines of chemistry, biochemistry, and biophysics depend on molecular interactions, including protein folding, drug design, pathogen detection, materials science, sensors, nanotechnology, etc. [3–7]. In ternary and binary liquid combinations, intermolecular interactions are crucial. The degree of connection in liquid mixtures was qualitatively assessed using the ultrasonic velocity of the liquid mixtures. Because there are numerous types of solvents or solvent mixes with acceptable qualities, utilizing mixed solvents in industrial and biological processes is more practical than using single solvents [7-9]. The intermolecular interactions of the medium determine reaction speeds and the stability of the intermediates generated.

In this investigation, the study of binary liquid mixtures of benzyl propionate and methanol systems of different molar

concentrations at different temperaturesis very helpful in the paint industry due to the wide usage of benzyl propionate and methanol in this.Calculating the various parameters, including acoustic impedance (Z), adiabatic compressibility (β_a), intermolecular free length (L_f), relaxation time (τ), internal pressure (π), Gibb's free energy (ΔG), and enthalpy (H), provided a thorough understanding of the molecular interactions between the solute and solvent. The intermolecular interactions that are present in the system and how they are impacted by variations in temperature and concentration are used to explain the plotted graphs.

Table 1. U, ρ, η, β_a, L_f and V_f of benzyl propionate with methanol

Mole fraction	Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^3 kg m^{-3}	Viscosity (η) 10^{-3} N s m^{-2}	Adiabatic compressibility (β_a) 10^{-10} m^2 N^{-1}	Free length (L_f) 10^{-10} m	Free volume (V_f) 10^{-6} m^3 mol^{-1}
Temperature 308 K						
0.000	1371	1.019	1.639	5.217	0.478	0.181
0.189	1368	0.983	1.459	5.435	0.488	0.168
0.418	1331	0.981	1.210	5.749	0.502	0.148
0.580	1313	0.955	1.043	6.067	0.515	0.130
0.788	1218	0.896	0.747	7.515	0.573	0.109
1.000	1076	0.783	0.416	11.015	0.694	0.082
Temperature 313 K						
0.000	1348	1.017	1.507	5.400	0.491	0.201
0.189	1320	0.981	1.312	5.841	0.510	0.187
0.418	1316	0.979	1.087	5.893	0.512	0.171
0.580	1274	0.953	0.942	6.463	0.537	0.145
0.788	1182	0.894	0.673	7.998	0.597	0.122
1.000	1041	0.779	0.381	11.832	0.726	0.092
Temperature 318 K						
0.000	1340	1.015	1.398	5.478	0.498	0.223
0.189	1316	0.978	1.217	5.899	0.517	0.208
0.418	1300	0.977	1.011	6.046	0.524	0.187
0.580	1260	0.951	0.859	6.619	0.548	0.164
0.788	1203	0.892	0.621	7.735	0.592	0.141
1.000	1037	0.776	0.356	11.979	0.737	0.101

Experimental Methods:

The mixtures of methanol and benzyl propionate ofvarious concentrations in mole fractions were prepared at room temperature. The instruments are cleaned with double-distilled water, which is then purified with acetone. Before carrying out the experiment, each of them is permitted to maintain a constant temperature by anelectronically operated digital constant temperature bath with an accuracy of $\pm$ 1 ^oC which is used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid. A 5 cc specific gravity bottle was used to measure the solutions' densities. The experimental mixture in the specific gravity bottle was placed in the temperature-controlled water bath. Using an electronic digital balance with an accuracy of 0.001 g, the sample's weight was determined. The viscosities of the binary mixes were determined using an Ostwald viscometer. Using a digital racing stopwatch with a 0.1-second precision, the flow time was

calculated. At a frequency of 2 MHz, the ultrasonic velocities of the binary mixes and the pure solvent were measured using a single-crystal variable path interferometer (Mittal Enterprises, New Delhi). The following relations were used to calculate the acoustic impedance (Z), adiabatic compressibility (β_a), intermolecular free length (L_f), relaxation time ($\boldsymbol{\tau}$), internal pressure (π), Gibb's free energy ($\boldsymbol{\Delta G}$) and enthalpy (H) from the measured density (ρ), viscosity (η) and ultrasonic velocity (U).

1. **Adiabatic compressibility (β_a)** $\beta_a = \frac{1}{U^2 \rho}$
2. **Intermolecular free length** $L_f = K_T \beta_a^{1/2}$
   $K_T = (93.875 + 0.375T) \times 10^{-8}$
3. **Free volume** $V_f = (\frac{M_{eff.}}{K\eta} U)^{3/2}$
4. **Internal pressure** $\pi_i = bRT \left(\frac{K\eta}{U}\right)^{\frac{1}{2}} (\rho^{\frac{2}{3}}/M_{eff}^{7/6})$
5. **Molar volume** $V_m = \frac{M}{\rho}$
6. **Acoustic Impedance** Z = Uρ
7. **Enthalpy** $H = \pi_i V_m$
8. **Relaxation time** $\tau = \frac{4}{3}\beta_a \eta$
9. **Gibb's free energy** $\Delta G = kT ln(kT\tau/h)$

Table 2. U, ρ, η, β_a, L_f and V_f of benzyl propionate with methanol

Mole fraction	Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^3 kg m^{-3}	Viscosity (η) 10^{-3} N s m^{-2}	Adiabatic compressibility (β_a) 10^{-10} m^2 N^{-1}	Free length (L_f) 10^{-10} m	Free volume (V_f) 10^{-6} m^3 mol^{-1}
Temperature 323 K						
0.000	1323	1.013	1.265	5.632	0.510	0.254
0.189	1309	0.974	1.120	5.986	0.526	0.234
0.418	1282	0.975	0.939	6.231	0.536	0.204
0.580	1254	0.949	0.801	6.697	0.556	0.180
0.788	1182	0.889	0.579	8.037	0.609	0.153
1.000	1018	0.773	0.326	12.464	0.759	0.113
Temperature 328 K						
0.000	1304	1.010	1.154	5.812	0.522	0.285
0.189	1293	0.972	1.050	6.144	0.537	0.253
0.418	1266	0.972	0.867	6.405	0.548	0.226
0.580	1239	0.947	0.746	6.876	0.568	0.197
0.788	1172	0.887	0.537	8.201	0.621	0.169
1.000	1004	0.769	0.301	12.900	0.778	0.124
Temperature 333 K						
0.000	1282	1.008	1.063	6.032	0.537	0.314
0.189	1274	0.968	0.965	6.354	0.551	0.281
0.418	1246	0.970	0.806	6.635	0.563	0.246
0.580	1218	0.944	0.706	7.134	0.584	0.209
0.788	1156	0.885	0.500	8.443	0.635	0.184
1.000	990	0.766	0.283	13.309	0.798	0.133

Table 3.π ,τ, ΔG , V_m, Z and H of benzyl propionate with methanol

Mole fraction	Internal Pressure (π) 10^6 N/m^2	Relaxation time (τ) 10^{-13} s	Gibb's Free Energy (ΔG) 10^{-21} J/mol	Molar Volume (V_m) 10^{-6} m^3 mol^{-1}	Acoustic impedance (Z) 10^6 kg m^{-2}s^{-1}	Enthalpy (H) kJ/mol
Temperature 308 K						
0.000	305.410	11.405	8.459	161.075	1.397	49.193
0.189	341.275	10.579	8.139	141.666	1.344	48.347
0.418	418.949	9.276	7.580	111.016	1.306	46.510
0.580	497.062	8.442	7.180	91.555	1.255	45.508
0.788	648.605	7.489	6.670	67.047	1.092	43.487
1.000	980.841	6.122	5.814	40.919	0.843	40.135
Temperature 313 K						
0.000	299.756	10.853	8.451	161.312	1.373	48.345
0.189	334.265	10.221	8.192	141.923	1.296	47.440
0.418	405.389	8.542	7.417	111.212	1.289	45.084
0.580	486.420	8.118	7.197	91.795	1.214	44.651
0.788	634.562	7.187	6.671	67.183	1.057	42.632
1.000	966.567	6.023	5.908	41.129	0.811	39.754
Temperature 318 K						
0.000	293.677	10.213	8.389	161.725	1.361	47.495
0.189	327.174	9.580	8.108	142.295	1.288	46.555
0.418	398.956	8.154	7.401	111.481	1.271	44.476
0.580	473.919	7.581	7.081	91.962	1.199	43.582
0.788	612.533	6.409	6.344	67.347	1.074	41.252
1.000	949.090	5.701	5.830	41.288	0.804	39.186

Table 4. π ,τ, ΔG , V_m, Z and H of benzyl propionate with methanol

Mole fraction	Internal Pressure (π) 10^6 N/m^2	Relaxation time (τ) 10^{-13} s	Gibb's Free Energy (ΔG) 10^{-21} J/mol	Molar Volume (V_m) 10^{-6} m^3 mol^{-1}	Acoustic impedance (Z) 10^6 kg m^{-2}s^{-1}	Enthalpy (H) kJ/mol
Temperature 323 K						
0.000	285.319	9.506	8.270	162.024	1.341	46.228
0.189	318.684	8.943	7.998	142.895	1.276	45.538
0.418	392.793	7.810	7.394	111.729	1.251	43.886
0.580	465.448	7.159	7.006	92.167	1.190	42.899
0.788	605.349	6.215	6.376	67.527	1.052	40.877
1.000	928.348	5.431	5.776	41.448	0.787	38.479
Temperature 328 K						
0.000	278.158	8.945	8.193	162.477	1.318	45.194
0.189	314.665	8.603	8.016	143.228	1.257	45.069
0.418	384.885	7.407	7.338	112.012	1.232	43.111
0.580	458.072	6.845	6.981	92.401	1.173	42.326
0.788	593.190	5.873	6.288	67.700	1.040	40.159
1.000	909.499	5.192	5.731	41.664	0.772	37.893
Temperature 333 K						
0.000	272.876	8.550	8.179	162.896	1.292	44.450
0.189	307.953	8.182	7.978	143.735	1.234	44.263
0.418	379.169	7.133	7.347	112.319	1.209	42.588
0.580	455.576	6.724	7.076	92.654	1.150	42.211
0.788	584.200	5.638	6.266	67.901	1.023	39.668
1.000	899.033	5.036	5.747	41.827	0.758	37.604

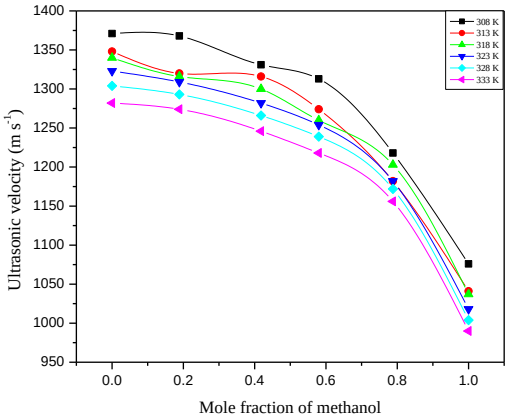

Figure1. Ultrasonic velocity

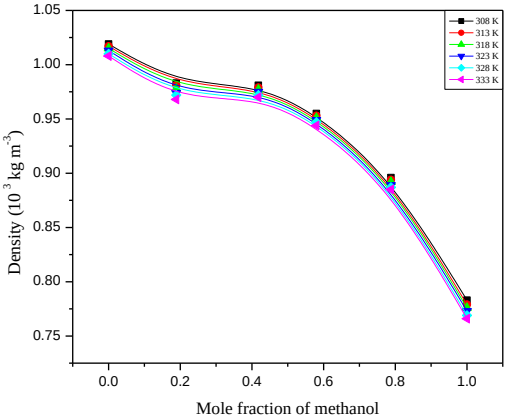

Figure2. Density

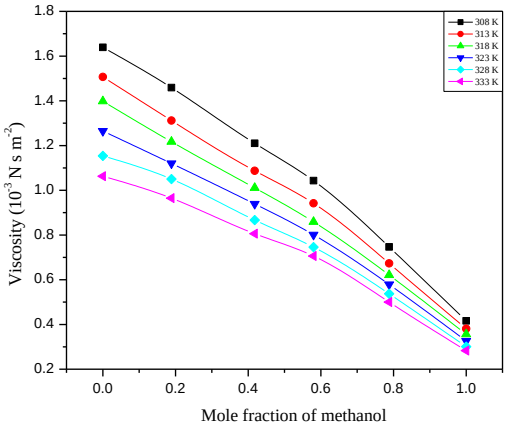

Figure3. Viscosity

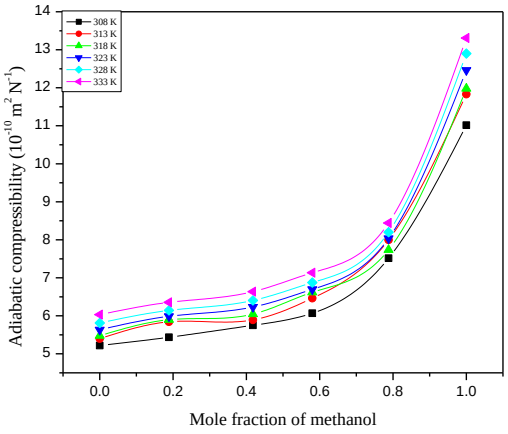

Figure4. Adiabatic compressibility

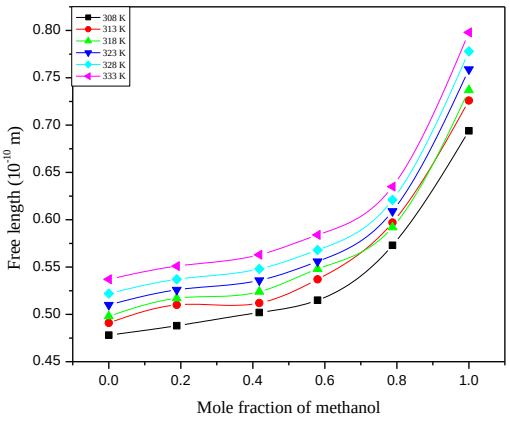

Figure5. Free length

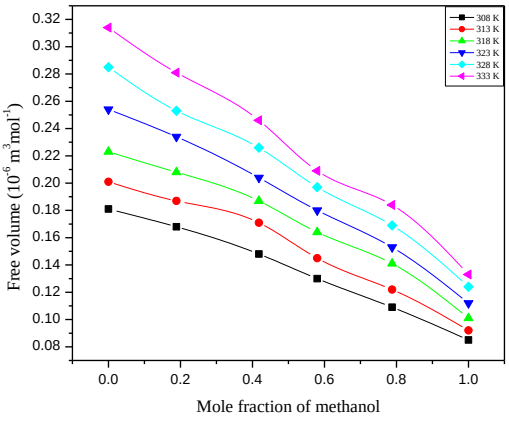

Figure6. Free volume

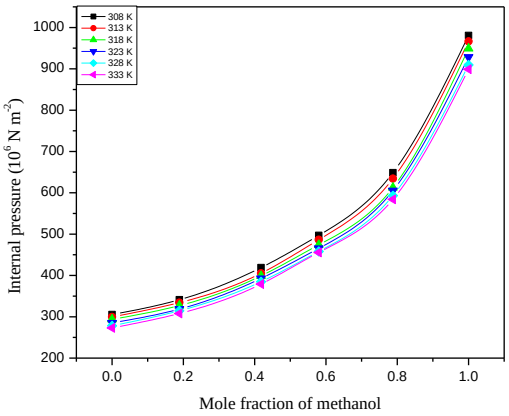

Figure7. Internal pressure

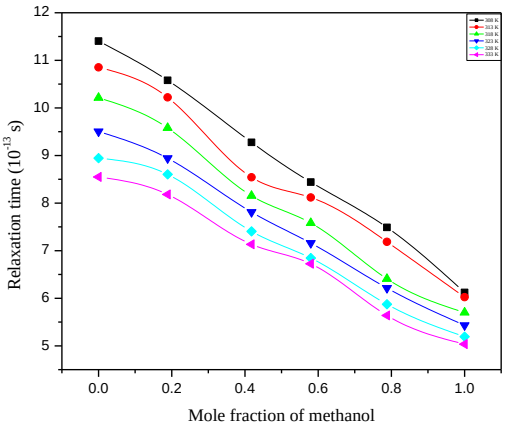

Figure8. Relaxation time

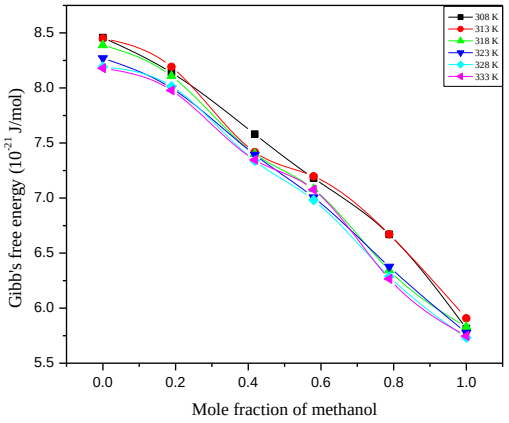

Figure9.Gibb's free energy

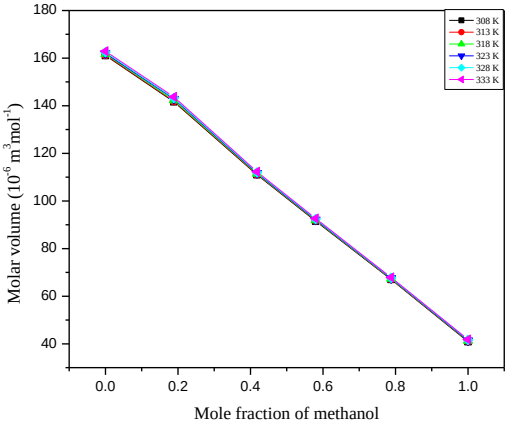

Figure10. Molar volume

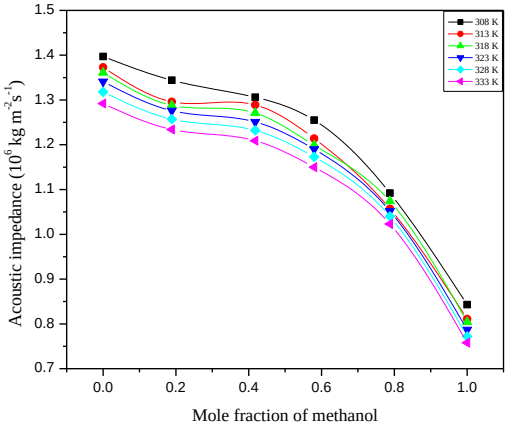

Figure11. Acoustic impedance

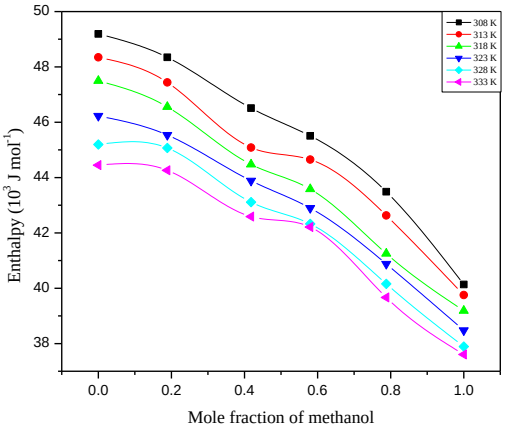

Figure l2. Enthalpy

The ultrasonic plots for benzyl propionate with methanol for varying temperatures from 308 K to 333 K and the entire range of composition are shown in Figure 1 to Figure 12. The following are the resulting discussions:

Ultrasonic velocity decreases with increasing concentration of methanol, also with increasing temperatures[10]. The velocity decreases indicating a decrease of thermal forces with temperature as well as with increasing concentration of methanol showing the strong interaction between solute and the solvent which depicts in Figure1.

Density being a physical parameter is purely dependent on the molecular weights of the combining molecules, hence is decreasing in nature. Viscosity starts with wider values at higher concentrations of benzyl propionate and ends with narrower values as it reaches the methanol full concentration. Viscosity is related to the molecular interaction between the components of the mixtures, as well as to the size and shape of molecules which are shown in Figure 3.

Adiabatic compressibility rules the velocity component as such it is the compressibility thatis the factor for the changes in the molecular structure which in turn changes the Ultrasonic Velocity. From Figure 4, it is quite evident that at all temperatures, the adiabatic compressibility increases[11]. Compressibility increase can be attributed to contraction on mixing of a binary mixture, which would lead to complex interaction.

Intermolecular free length is the intermolecular distance between the molecules, increasing as the compressibility of the mixture increases. From different interpretations of the previous study undertaken, this principle is also in good agreement with the literature papers[12-14], that is as Ultrasonic velocity decreases, Intermolecular free length increases and vice versa. Free Volume decreases as intermolecular length increases at all temperature changes.When and if a liquid or liquid combination experiences an isothermal shift that is equivalent to or barely detectable, internal pressure is used to assess the change in internal energy. Additionally, it represents the cohesive or binding forces between the molecules of the solvent and the solute. The internal pressure in the current system is trending upward. This might be brought on by a modification in the intermolecular configuration, as seen in Figure 7. The inter-proton distance between adjacent molecules normally increases with an increase in molar concentration, which is also a result of the weakening of intermolecular interactions, which causes the decrease in apparent ultrasonic absorption.

An unusual method of examining intermolecular interactions is acoustic impedance. Temperature and mole fraction both cause a drop in it. As a result, the specific acoustic impedance depends on the molecular packing of the medium as well as the different liquid structures. When and if a liquid or liquid combination experiences an isothermal shift that is equivalent to or barely detectable, internal pressure is used to assess the change in internal energy. Additionally, it represents the cohesive or binding forces between the molecules of the solvent and the solute. The internal pressure in the current system is trending upward. A shift in the intermolecular arrangement may be the cause of this. This system's enthalpy and Gibbs free energy drop as the mole fraction increases. The mobility of the medium is measured by Gibb's free energy. The entropy will be higher and the free energy will be lower the more mobile the medium is. As concentration rises, it has been seen that Gibb's free energy falls, indicating that the mixture is more mobile, as seen in Figures 9 and 12.

Conclusion:

It is determined that there is significant molecular interaction between the components of mixing based on experimentally determined and assessed parameters for binary systems. The presence of solute-solvent interactions leading to attractive forces improves the tendency for structures to form, whereas dipole-dipole and dipole-induced dipole enhance the features of mixes that break up structures. With a rise in methanol concentration, there is a noticeable interaction between the solvent and the

solute. However, when the temperature rises, the contact between the solute and solvent weakens. Previous reports of similar interactions confirm the findings of the present investigation.

Conflict of Interest

The authors declare no conflict of interest.

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