

Ultrasonic and Thermodynamic Characterization of Ethyl Benzoate with Branched Butanol Isomers

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Abstract: Ultrasonic velocity, density, and viscosity measurements were performed for binary mixtures of ethyl benzoate with 2-methyl-1-propanol and 2-methyl-2-propanol over the full mole fraction range at temperatures from 303.15 to 318.15 K. Thermo-acoustic parameters including molar volume, adiabatic compressibility, intermolecular free length, internal pressure, acoustic impedance, and enthalpy were derived from the experimental data to evaluate intermolecular interactions. Composition dependent variations reveal non-ideal behaviour in both systems. Increasing ester concentration enhances ultrasonic velocity and acoustic impedance while reducing compressibility and free length, indicating strengthened cohesive forces and reduced molecular free volume. The mixture containing 2-methyl-1-propanol demonstrates comparatively stronger interaction effects than the corresponding tert-butanol system, attributed to lower steric obstruction and more effective hydrogen bonding with the ester carbonyl group. Temperature elevation weakens structural organization in both mixtures. The comparative analysis highlights the influence of alcohol branching on acoustic response and thermodynamic behaviour in ester-alcohol systems, providing useful experimental benchmarks for theoretical modelling and industrial formulation design.

Keywords: Ultrasonic and Thermodynamic Characterization of Ethyl Benzoate with Branched Butanol Isomers

I. INTRODUCTION

Acoustic methods have long been recognized as effective tools for probing liquid structure and intermolecular behaviour. Since early theoretical developments in liquid acoustics [1], correlations between ultrasonic velocity and thermodynamic properties have been used to examine molecular association and packing effects in binary systems [2]–[5]. The sensitivity of sound propagation to compressibility enables detailed analysis of cohesive forces operating within mixtures [3]–[6].

Derived parameters such as adiabatic compressibility and intermolecular free length provide insight into microscopic structural changes occurring during mixing [6]–[8]. Variations in these quantities with temperature and composition are frequently associated with hydrogen bonding rearrangements and dipolar interactions [9]–[12].

Aromatic esters such as ethyl benzoate possess polar carbonyl groups capable of interacting with protic solvents through specific and non-specific forces [13], [14]. When combined with alcohols, the extent of interaction depends significantly on molecular architecture. Primary branched alcohols allow relatively unhindered access to the hydroxyl group, whereas tertiary alcohols exhibit steric shielding that may limit effective association [15], [16].

Previous investigations of ester-alcohol mixtures have reported measurable deviations from ideal mixing behaviour in terms of excess molar volume and compressibility [17]–[19]. Ultrasonic and density studies on related systems have further demonstrated the importance of molecular shape in determining acoustic response [20], [21]. Recent publications (2023–2025) emphasize the continued relevance of thermo-acoustic measurements for validating predictive thermodynamic models [22]–[25].



However, direct comparison between ethyl benzoate mixed with 2-methyl-1-propanol and with 2-methyl-2-propanol across multiple temperatures has received limited attention. The present investigation addresses this gap by systematically analyzing both systems under identical experimental conditions.

II. MATERIALS AND METHODS

2.1 Materials

Ethylbenzoate, 2-methyl-1-propanol (isobutanol), and 2-methyl-2-propanol (tert-butanol) of analytical reagent grade were used without further purification. Prior to use, the purity of each component was confirmed by comparison of measured density and viscosity of pure liquids with literature values at the same temperature. Commercially supplied samples were stored in tightly sealed brown bottles to prevent moisture absorption and evaporation.

2.2 Preparation of mixtures

Binary mixtures of EB + 2-methyl-1-propanol and EB + 2-methyl-2-propanol were prepared by mass mixing over the entire mole-fraction range of ethylbenzoate ($X_{EB} = 0.0000$ to $X_{EB} = 1.0000$) in steps of 0.06–0.10. All measurements were performed at least in triplicate, and the average value was used for subsequent calculations.

2.3 Experimental techniques

1. Density:

Densities were measured using an oscillating-tube densimeter, calibrated with doubly distilled water and dry air. The instrument was thermostatted at ± 0.01 K over the temperature range 303.15 to 318.15 K.

2. Ultrasonic

velocity:

Ultrasonic velocity was determined using a ultrasonic interferometer operating at 2 MHz, connected to a thermostatted water bath. The temperature of the liquid cell was maintained within ± 0.05 K.

3. Viscosity:

Dynamic viscosity was measured with a capillary viscometer in a thermostated bath. The apparatus was calibrated with standard reference liquids (e.g., purified water, glycerol) to ensure accuracy.

2.4 Computation of derived parameters

From the experimental data of ultrasonic velocity U (m/s), density ρ (kg/m³), and viscosity η (mPa·s), the following parameters were computed.

- **Molar volume:** $V = \frac{M}{\rho}$, where M is the molar mass of the mixture.
- **Adiabatic compressibility:** $\beta_{ad} = \frac{1}{\rho U^2}$.
- **Intermolecular free length:** $L_f = \frac{k}{\rho^{1/2}}$, where k is a temperature-dependent constant obtained from the correlation with pure liquids.
- **Internal pressure:** $p = \frac{U^2}{v}$ (approximate form based on ultrasonic and molar-volume data).
- **Acoustic impedance:** $Z = \rho U$.
- **Molar enthalpy:** estimated from the velocity–density–temperature dependence using empirical thermodynamic relations suited to ester–alcohol mixtures.

Excess quantities (e.g., excess molar volume, excess viscosity, excess enthalpy) were fitted using the **Redlich–Kister polynomial equation** to obtain interaction coefficients and standard deviations.



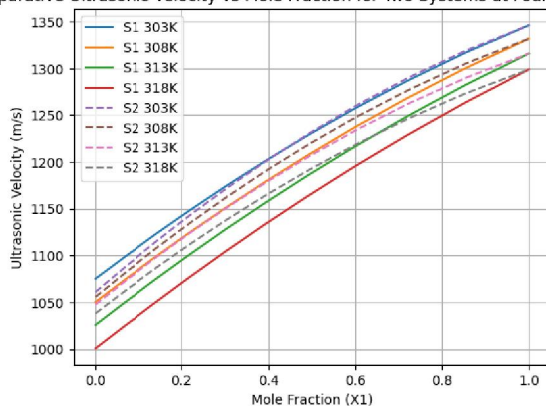
III. RESULTS AND DISCUSSION

3.1. Ultrasonic Velocity Behaviour

In both mixtures, ultrasonic velocity increases progressively with ethyl benzoate mole fraction, indicating enhanced cohesive interactions as ester content rises [10], [20]. This effect is consistent across all temperatures studied. The 2-methyl-1-propanol system displays slightly higher velocity values at comparable compositions, suggesting more efficient intermolecular association relative to the tert-butanol system.

An increase in temperature leads to systematic velocity reduction, reflecting thermal expansion and weakening of intermolecular attraction [4], [23].

Comparative Ultrasonic Velocity vs Mole Fraction for Two Systems at Four Temperatures

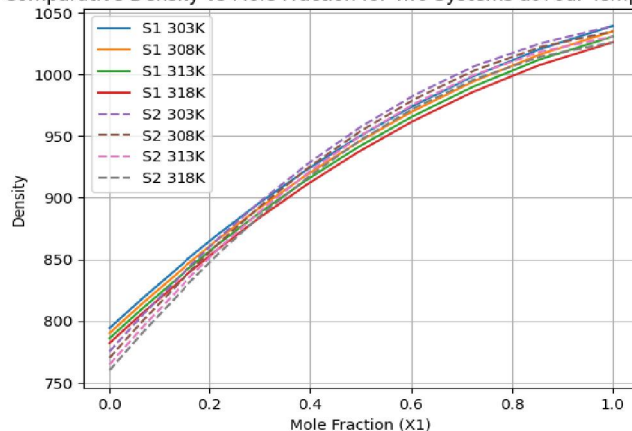


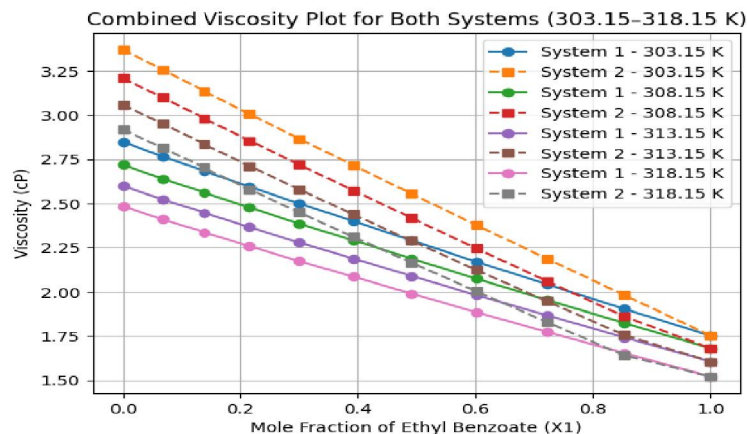
3.2. Density and Viscosity Trends

Density increases nearly linearly with ester concentration, confirming improved packing efficiency of the aromatic component within the mixture [11]. Viscosity decreases with temperature for both systems due to diminished intermolecular resistance.

Notably, mixtures containing 2-methyl-2-propanol exhibit higher viscosities at lower ester fractions, which can be attributed to pronounced self-association and steric constraints characteristic of tertiary alcohols [15].

Comparative Density vs Mole Fraction for Two Systems at Four Temperatures





3.3. Adiabatic Compressibility and Free Length

Adiabatic compressibility decreases with increasing ester fraction, indicating reduction in free volume and stronger intermolecular cohesion [6], [19]. Correspondingly, intermolecular free length follows a decreasing trend. Comparative analysis reveals slightly lower compressibility values in the 2-methyl-1-propanol system, reinforcing the conclusion of stronger interaction strength.

Table 1
Ethylbenzoate(X_1) + 2-methyl-1-propanol(X_2)
Ultrasonic velocities, Densities, Viscosities and related Acoustic Parameters

Mole fraction X_1	Velocity (U) m/s	Density (ρ) $\times 10^{-3}$ gm/cm ³	Viscosity (η) cP	Mol.Vol. V cm ³ mol ⁻¹	Ad. Comp. $\beta_{ad} \times 10^{-12}$ m ² N ⁻¹	Int Mol. Free Length $L_f(A)$	internal pressure π Nm ⁻²	Acoustic impedance (Z) Kg m ⁻² s ⁻¹	Enthalpy H Jmol ⁻¹
303.15K									
0.0000	1075.2	794.20	2.8500	93.3266	14.5562	0.7572	9.7435	853.92	909.32
0.0670	1098.4	819.00	2.7660	96.7178	14.7312	0.7617	8.9706	899.59	867.61
0.1390	1122.6	844.40	2.6840	100.2984	14.9246	0.7667	8.2509	947.92	827.55
0.2168	1147.7	870.20	2.5950	104.1213	15.1369	0.7721	7.5664	998.73	787.82
0.3010	1173.8	896.30	2.5000	108.2326	15.3722	0.7781	6.9162	1052.08	748.56
0.3924	1200.9	922.50	2.4010	112.6964	15.6332	0.7847	6.3009	1107.83	710.09
0.4921	1228.8	948.40	2.2910	117.6102	15.9210	0.7919	5.7095	1165.39	671.49
0.6011	1257.6	973.80	2.1710	123.0584	16.2411	0.7998	5.1428	1224.65	632.87
0.7209	1286.9	997.90	2.0440	129.2181	16.5960	0.8085	4.6031	1284.20	594.81
0.8532	1316.6	1020.10	1.9030	136.2677	16.9928	0.8181	4.0821	1343.06	556.26
1.0000	1346.2	1039.20	1.7510	144.5054	17.4389	0.8288	3.5827	1398.97	517.72
308.15K									
0.0000	1050.3	790.10	2.4380	93.8109	13.9619	0.7416	9.0865	829.84	852.41
0.0670	1073.9	815.00	2.3460	97.1925	14.1504	0.7466	8.3279	875.23	809.41
0.1390	1098.4	840.30	2.2690	100.7878	14.3578	0.7520	7.6445	922.99	770.47
0.2168	1124.1	866.10	2.1910	104.6142	14.5895	0.7580	7.0030	973.58	732.62
0.3010	1150.8	892.20	2.1100	108.7300	14.8435	0.7646	6.3975	1026.74	695.60
0.3924	1178.7	918.40	2.0300	113.1995	15.1278	0.7719	5.8307	1082.52	660.03
0.4921	1207.6	944.30	1.9420	118.1208	15.4432	0.7799	5.2873	1140.34	624.54



0.6011	1237.6	969.60	1.8540	123.5915	15.7968	0.7888	4.7770	1199.98	590.40
0.7209	1268.4	993.70	1.7710	129.7643	16.1904	0.7986	4.3037	1260.41	558.47
0.8532	1300.0	1015.80	1.6820	136.8446	16.6371	0.8095	3.8513	1320.54	527.03
1.0000	1331.9	1034.80	1.5960	145.1198	17.1430	0.8217	3.4291	1378.25	497.63

313.15K

0.0000	1025.8	786.00	2.1100	94.3003	13.3876	0.7262	8.6622	806.28	816.85
0.0670	1049.6	810.90	2.0040	97.6839	13.5856	0.7315	7.8854	851.12	770.28
0.1390	1074.4	836.20	1.9340	101.2820	13.8045	0.7374	7.2282	898.41	732.09
0.2168	1100.5	862.10	1.8680	105.0996	14.0483	0.7439	6.6208	948.74	695.84
0.3010	1127.8	888.20	1.8060	109.2196	14.3203	0.7510	6.0576	1001.71	661.61
0.3924	1156.2	914.30	1.7400	113.7072	14.6210	0.7589	5.5224	1057.11	627.93
0.4921	1186.0	940.30	1.6760	118.6233	14.9590	0.7676	5.0226	1115.20	595.79
0.6011	1216.9	965.50	1.6110	124.1163	15.3376	0.7772	4.5507	1174.92	564.81
0.7209	1249.0	989.60	1.5570	130.3019	15.7640	0.7880	4.1212	1236.01	537.00
0.8532	1282.1	1011.80	1.5000	137.3856	16.2461	0.7999	3.7120	1297.23	509.97
1.0000	1316.0	1030.60	1.4550	145.7112	16.8043	0.8136	3.3382	1356.27	486.41

318.15K

0.0000	1000.7	782.10	1.6220	94.7705	12.8040	0.7101	7.7863	782.65	737.91
0.0670	1024.6	807.00	1.5180	98.1560	13.0087	0.7158	7.0344	826.85	690.47
0.1390	1049.7	832.40	1.4640	101.7443	13.2373	0.7221	6.4445	873.77	655.69
0.2168	1076.3	858.20	1.4180	105.5772	13.4983	0.7291	5.9082	923.68	623.77
0.3010	1104.2	884.20	1.3790	109.7137	13.7894	0.7370	5.4186	976.33	594.50
0.3924	1133.4	910.40	1.3460	114.1943	14.1102	0.7455	4.9698	1031.85	567.52
0.4921	1163.9	936.30	1.3080	119.1301	14.4683	0.7549	4.5376	1089.76	540.56
0.6011	1195.8	961.50	1.2880	124.6327	14.8719	0.7654	4.1587	1149.76	518.31
0.7209	1228.9	985.40	1.2880	130.8573	15.3257	0.7769	3.8283	1210.96	500.96
0.8532	1263.3	1007.30	1.2980	137.9993	15.8436	0.7900	3.5236	1272.52	486.26
1.0000	1299.0	1026.00	1.3430	146.3645	16.4464	0.8048	3.2698	1332.77	478.59

Table 2
Ethylbenzoate(X₁) + 2-methyl-2-propanol(X₂)
Ultrasonic velocities, Densities, Viscosities and related Acoustic Parameters

Mole fraction X ₁	Velocity (U) m/s	Density (ρ)X10 ⁻³ gm/cm ³	Viscosity (η) cP	Mol. Vol. V cm ³ mol ⁻¹	Ad. Comp. β _{ad} ×10 ⁻¹² m ² N ⁻¹	Int Mol. Free Length L _f (Å)	internal pressure π Nm ⁻²	Acoustic impedance (Z) Kg m ⁻² s ⁻¹	Enthalpy H Jmol ⁻¹
303.15K									
0.0000	1061.0	775.30	3.3720	95.6017	14.5198	0.7562	10.50	822.59	1003.72
0.0685	1087.8	806.20	3.2580	98.3969	14.6776	0.7603	9.66	876.98	950.95
0.1419	1115.4	837.10	3.1360	101.4373	14.8622	0.7651	8.87	933.70	899.62
0.2209	1143.7	868.10	3.0060	104.7339	15.0680	0.7704	8.11	992.85	849.60
0.3061	1172.6	898.70	2.8670	108.3744	15.2998	0.7763	7.39	1053.82	800.79
0.3982	1202.0	928.40	2.7170	112.4518	15.5623	0.7829	6.70	1115.94	752.90
0.4981	1231.7	956.90	2.5550	117.0439	15.8542	0.7902	6.03	1178.61	705.71



0.6069	1261.4	983.30	2.3790	122.3151	16.1815	0.7983	5.39	1240.33	658.95
0.7258	1290.8	1006.70	2.1890	128.4527	16.5508	0.8074	4.77	1299.45	612.53
0.8562	1319.3	1025.00	1.9810	135.7191	16.9661	0.8175	4.17	1353.47	565.74
1.0000	1346.2	1039.20	1.7510	144.5054	17.4389	0.8288	3.58	1398.97	517.72
308.15K									
0.0000	1055.7	770.10	2.5890	96.2472	14.4722	0.7550	9.18	812.99	883.68
0.0685	1081.5	801.40	2.5150	98.9862	14.5950	0.7582	8.48	866.71	839.61
0.1419	1108.1	832.70	2.4390	101.9733	14.7458	0.7621	7.82	922.71	797.38
0.2209	1135.3	864.00	2.3590	105.2309	14.9179	0.7665	7.19	980.90	756.60
0.3061	1163.2	894.90	2.2730	108.8346	15.1194	0.7717	6.59	1040.95	716.91
0.3982	1191.6	924.90	2.1810	112.8774	15.3520	0.7776	6.01	1102.11	678.35
0.4981	1220.3	953.50	2.0810	117.4613	15.6175	0.7843	5.45	1163.56	640.62
0.6069	1249.1	979.90	1.9740	122.7395	15.9226	0.7919	4.92	1223.99	603.89
0.7258	1277.6	1003.20	1.8590	128.9008	16.2706	0.8005	4.41	1281.69	568.04
0.8562	1305.5	1022.10	1.7340	136.2236	16.6748	0.8104	3.91	1334.35	532.75
1.0000	1331.9	1034.80	1.5960	145.1198	17.1430	0.8217	3.43	1378.25	497.63
313.15K									
0.0000	1047.6	764.80	2.0460	96.9142	14.3497	0.7518	8.29	801.20	803.24
0.0685	1072.6	796.40	1.9990	99.6077	14.4459	0.7543	7.68	854.22	765.43
0.1419	1098.3	828.10	1.9520	102.5397	14.5666	0.7575	7.11	909.50	729.49
0.2209	1124.7	859.70	1.9020	105.7573	14.7139	0.7613	6.57	966.90	694.80
0.3061	1151.7	890.90	1.8500	109.3232	14.8885	0.7658	6.05	1026.05	661.53
0.3982	1179.2	921.10	1.7950	113.3430	15.0962	0.7711	5.55	1086.16	629.53
0.4981	1207.1	949.80	1.7360	117.9189	15.3410	0.7773	5.08	1146.50	598.62
0.6069	1235.2	976.30	1.6720	123.1921	15.6276	0.7846	4.62	1205.93	568.67
0.7258	1263.0	999.60	1.6050	129.3651	15.9581	0.7928	4.18	1262.49	540.11
0.8562	1290.1	1018.30	1.5340	136.7320	16.3445	0.8023	3.75	1313.71	512.88
1.0000	1316.0	1030.60	1.4550	145.7112	16.8043	0.8136	3.34	1356.27	486.41
318.15K									
0.0000	1038.1	760.00	1.6890	97.5263	14.1796	0.7473	7.65	788.96	746.41
0.0685	1062.3	792.00	1.6570	100.1610	14.2485	0.7491	7.12	841.34	712.75
0.1419	1087.1	823.90	1.6270	103.0624	14.3438	0.7516	6.61	895.66	681.26
0.2209	1112.7	855.80	1.5970	106.2392	14.4672	0.7549	6.13	952.25	651.29
0.3061	1138.9	887.20	1.5660	109.7792	14.6201	0.7588	5.67	1010.43	622.68
0.3982	1165.6	917.50	1.5330	113.7878	14.8079	0.7637	5.23	1069.44	595.28
0.4981	1192.7	946.30	1.4990	118.3550	15.0326	0.7695	4.81	1128.65	569.24
0.6069	1220.0	972.80	1.4630	123.6353	15.3002	0.7763	4.40	1186.82	544.44
0.7258	1247.1	995.90	1.4250	129.8457	15.6166	0.7843	4.01	1241.99	520.98
0.8562	1273.6	1014.30	1.3860	137.2712	15.9919	0.7936	3.64	1291.81	499.15
1.0000	1299.0	1026.00	1.3430	146.3645	16.4464	0.8048	3.27	1332.77	478.59

3.4. Internal Pressure and Acoustic Impedance

Internal pressure increases as ester concentration rises, suggesting greater cohesive energy density within the mixture [17]. Acoustic impedance follows a similar pattern due to concurrent increases in velocity and density.

The reduced interaction efficiency in the tert-butanol system can be attributed to steric hindrance around the hydroxyl group, limiting effective interaction with the ester carbonyl [16], [24].



3.5. Structural Implications

The comparative behaviour of these systems highlights the importance of molecular architecture in determining liquid mixture properties. Reduced steric hindrance in 2-methyl-1-propanol facilitates closer molecular approach and stronger associative interactions.

IV. CONCLUSION

Comprehensive thermo-acoustic evaluation demonstrates distinct interaction differences between ethyl benzoate mixtures with primary and tertiary branched alcohols. The 2-methyl-1-propanol system shows stronger intermolecular cohesion, lower compressibility, and tighter structural organization compared to the tert-butanol analogue. Temperature increase reduces cohesive forces in both systems.

The findings underline the critical influence of steric effects on acoustic and thermodynamic behavior in ester-alcohol mixtures and provide reliable experimental data for theoretical modeling and industrial formulation development.

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