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Comparative Ultrasonic and Thermophysical Investigation of Ethylbenzoate + Alcohol Binary Liquid Mixtures

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Abstract
Ultrasonic velocity, density and viscosity measurements provide valuable information regarding molecular interactions and structural effects in liquid mixtures. In the present investigation, ultrasonic velocity (U), density (ρ), viscosity (η) and derived acoustic parameters such as adiabatic compressibility (β_ad), intermolecular free length (L_f), acoustic impedance (Z), internal pressure (π), molar volume (V_m) and enthalpy (H) have been determined for binary liquid mixtures of ethylbenzoate with 2-methyl-1-propanol and 2-butanol over the entire mole fraction range at temperatures of 303.15-318.15 K. Ultrasonic and thermophysical parameters exhibit systematic dependence on composition and temperature, revealing significant deviation from ideal behavior. Excess properties were evaluated to quantify the strength of intermolecular interactions. The comparative analysis indicates stronger interaction effects in the ethylbenzoate + 2-butanol system relative to the branched alcohol system, attributed to molecular geometry and hydrogen bonding efficiency. The results demonstrate that ultrasonic techniques are effective probes for investigating molecular interactions in ester-alcohol mixtures and provide reliable data for thermodynamic modeling and industrial applications.

Keywords: Ultrasonic velocity, Binary liquid mixtures, Excess properties, Acoustic parameters, Molecular interactions, Ethylbenzoate

1. Introduction
The study of thermophysical and acoustic properties of binary liquid mixtures has long been recognized as an important tool for understanding molecular interactions and liquid structure [1-3]. Early theoretical foundations on molecular interactions and liquid behavior were established through classical works on polar molecules and kinetic theory of liquids [1, 2]. Ultrasonic techniques have since emerged as sensitive and non-destructive methods for investigating intermolecular forces, packing efficiency and structural rearrangements in liquid mixtures [4, 5].
Ultrasonic velocity is directly related to density and compressibility, and therefore provides insight into the elastic properties of liquids and liquid mixtures [6-8]. Deviations of acoustic and thermodynamic properties from ideal behavior often indicate the presence of specific interactions such as hydrogen bonding, dipole-dipole interactions and dispersive forces [9], [10]. Ester-alcohol systems are particularly interesting because they involve competing interactions between polar functional groups and non-polar hydrocarbon chains [11, 12].
Several researchers have reported ultrasonic, volumetric and excess thermodynamic properties of organic binary mixtures containing alcohols, esters and ketones [13-16]. These studies demonstrate that molecular structure, chain length and branching significantly influence interaction strength and acoustic behavior [17, 18]. Linear alcohols generally exhibit stronger association compared to branched alcohols due to more effective hydrogen bonding and molecular packing [19, 20].
Despite extensive studies on various ester-alcohol mixtures, systematic comparative investigations on ethylbenzoate with both branched and linear alcohols over a wide temperature range remain limited. Ethylbenzoate is an aromatic ester of industrial relevance, while 2-methyl-1-propanol and 2-butanol differ in molecular geometry and hydrogen bonding capability. Comparative ultrasonic studies of these systems can therefore provide

deeper insight into structure-property relationships in liquid mixtures [21-23].

The present work aims to experimentally determine ultrasonic velocity, density and viscosity for ethylbenzoate+2-methyl-1-propanol and ethylbenzoate +2-butanol mixtures at four temperatures. Derived acoustic and excess parameters are analyzed to elucidate the nature and strength of molecular interactions, with particular emphasis on comparative behavior between branched and linear alcohol systems [24-30].

2. Materials and Methods

High-purity analytical grade ethylbenzoate, 2-methyl-1-propanol and 2-butanol were used without further purification. Binary mixtures were prepared gravimetrically using an electronic balance with an uncertainty of ±0.0002 in mole fraction. Density was measured using a vibrating-tube densitometer, while viscosity measurements were performed using an Ubbelohde viscometer following standard procedures reported in the literature [10, 18]. Ultrasonic velocity measurements were carried out using a single-crystal ultrasonic interferometer operating at 3 MHz. Temperature control was maintained within ±0.1 K using a thermostatically controlled circulating water bath [6, 15].

3. Theoretical Relations and Excess Properties

The adiabatic compressibility (β_ad) was calculated using the relation [8]:

$$\beta_{ad} = \frac{1}{U^2 \rho}$$

Intermolecular free length (L_f) was obtained from Jacobson's relation [9]:

$$L_f = K\sqrt{\beta_{ad}}$$

Acoustic impedance (Z) was evaluated using [7]:

$$Z = U\rho$$

Excess properties (Y^E) were calculated to assess non-ideal behavior using the standard relation [14, 21]:

$$Y^E = Y - (X_1 Y_1 + X_2 Y_2)$$

4. Results and Discussion

The experimental ultrasonic velocity (U), density (ρ), and viscosity (η) data for the binary systems, ethyl benzoate + 2-methyl-1-propanol and ethyl benzoate + 2-butanol, were used to compute several thermoacoustic parameters, the values of which are presented in Table1 and Table2. The variation of these parameters with mole fraction and temperature provides important insight into the strength and nature of intermolecular interactions present in the system

4.1 Ultrasonic velocity

Ultrasonic velocity values increase progressively with increasing mole fraction of alcohol for both systems at all temperatures, indicating enhanced molecular packing and reduced free volume upon mixing [11, 13]. The increase in velocity is more pronounced in the ethylbenzoate + 2-butanol system, suggesting stronger intermolecular interactions compared to the branched alcohol system [18, 20].

4.2 Density

Density exhibits similar compositional dependence, confirming the formation of more compact molecular arrangements due to specific interactions between unlike molecules [10, 19]. Viscosity decreases with increasing temperature as thermal agitation weakens cohesive forces, while its variation with composition reflects changes in molecular association and structural organization [15, 17].

4.3 Adiabatic compressibility

Adiabatic compressibility decreases with increasing alcohol concentration, indicating reduced compressibility and increased rigidity of the liquid structure [8, 23]. Negative excess compressibility values observed throughout the composition range suggest strong attractive interactions between ethylbenzoate and alcohol molecules [14, 22]. The magnitude of excess deviations is higher for the 2-butanol system, attributed to its linear molecular structure allowing more effective hydrogen bonding and dipole alignment [20, 25].

4.4 Intermolecular free length

Intermolecular free length decreases with increasing alcohol content, further supporting the formation of tightly packed molecular structures [9, 16]. Acoustic impedance increases with mole fraction, reflecting enhanced resistance to sound propagation due to increased density and interaction strength [7, 24].

Table 1: Ethylbenzoate(X1) + 2-methyl-1-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. $\beta_{ad}\times10^{-12}$ 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-butanol(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. $\beta_{ad}\times10^{-12}$ 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}
s					**303.15K**				
0.0000	1152.0	798.20	2.595	92.859	16.626	0.8092	9.0122	919.53	836.866
0.0666	1171.1	823.70	2.537	96.137	16.650	0.8098	8.3550	964.64	803.224
0.1384	1190.7	849.70	2.474	99.619	16.685	0.8107	7.7287	1011.74	769.925
0.2159	1210.7	876.00	2.407	103.358	16.733	0.8118	7.1325	1060.57	737.197
0.2999	1231.1	902.40	2.335	107.412	16.795	0.8133	6.5626	1110.94	704.901
0.3912	1251.6	928.70	2.257	111.846	16.868	0.8151	6.0170	1162.36	672.974
0.4908	1272.1	954.50	2.173	116.758	16.954	0.8172	5.4939	1214.22	641.465
0.5999	1292.3	979.30	2.082	122.274	17.053	0.8196	4.9914	1265.55	610.312
0.7199	1311.8	1002.40	1.982	128.561	17.167	0.8223	4.5062	1314.95	579.320

0.8526	1330.1	1022.60	1.873	135.888	17.301	0.8255	4.0374	1360.16	548.635
1.0000	1346.2	1039.20	1.751	144.505	17.439	0.8288	3.5827	1398.97	517.723
					308.15K				
0.0000	1142.5	793.30	2.150	93.432	16.454	0.8050	8.2035	906.35	766.471
0.0666	1161.0	819.20	2.108	96.665	16.454	0.8050	7.6211	951.09	736.691
0.1384	1180.0	845.40	2.066	100.126	16.470	0.8054	7.0707	997.57	707.960
0.2159	1199.4	871.60	2.021	103.880	16.505	0.8063	6.5443	1045.40	679.820
0.2999	1219.1	898.10	1.974	107.926	16.548	0.8073	6.0444	1094.87	652.344
0.3912	1239.0	924.60	1.922	112.342	16.603	0.8087	5.5642	1145.58	625.096
0.4908	1259.0	950.40	1.867	117.262	16.678	0.8105	5.1042	1196.55	598.530
0.5999	1278.7	975.30	1.808	122.775	16.765	0.8126	4.6633	1247.12	572.533
0.7199	1297.9	998.50	1.743	129.063	16.871	0.8152	4.2373	1295.95	546.882
0.8526	1315.8	1018.70	1.673	136.408	16.995	0.8182	3.8267	1340.41	521.991
1.0000	1331.9	1034.80	1.596	145.120	17.143	0.8217	3.4291	1378.25	497.628
					313.15K				
0.0000	1137.5	789.50	1.734	93.882	16.389	0.8034	7.4792	898.06	702.165
0.0666	1155.0	815.60	1.709	97.092	16.356	0.8026	6.9709	942.02	676.822
0.1384	1172.9	841.90	1.686	100.542	16.340	0.8022	6.4927	987.46	652.790
0.2159	1191.2	868.30	1.663	104.275	16.342	0.8023	6.0382	1034.32	629.631
0.2999	1209.9	894.80	1.637	108.324	16.360	0.8027	5.6011	1082.62	606.730
0.3912	1228.7	921.00	1.612	112.781	16.392	0.8035	5.1866	1131.63	584.952
0.4908	1247.5	946.70	1.584	117.720	16.439	0.8047	4.7873	1181.01	563.559
0.5999	1266.1	971.40	1.555	123.268	16.502	0.8062	4.4049	1229.89	542.984
0.7199	1284.1	994.70	1.524	129.556	16.577	0.8080	4.0378	1277.29	523.119
0.8526	1301.0	1014.90	1.491	136.919	16.678	0.8105	3.6828	1320.38	504.245
1.0000	1316.0	1030.60	1.455	145.711	16.804	0.8136	3.3382	1356.27	486.414
					318.15K				
0.0000	1132.8	785.50	1.395	94.360	16.337	0.8022	6.8065	889.81	642.267
0.0666	1149.2	812.20	1.384	97.498	16.260	0.8003	6.3716	933.38	621.225
0.1384	1165.9	838.60	1.376	100.938	16.209	0.7990	5.9614	977.72	601.730
0.2159	1183.1	864.80	1.371	104.697	16.186	0.7984	5.5741	1023.14	583.585
0.2999	1200.5	891.10	1.366	108.774	16.173	0.7981	5.2041	1069.77	566.069
0.3912	1218.1	917.10	1.362	113.261	16.179	0.7983	4.8509	1117.12	549.416
0.4908	1235.6	942.80	1.357	118.207	16.193	0.7986	4.5109	1164.92	533.224
0.5999	1252.9	967.50	1.354	123.765	16.225	0.7994	4.1867	1212.18	518.166
0.7199	1269.6	990.60	1.350	130.093	16.272	0.8006	3.8723	1257.67	503.754
0.8526	1285.2	1010.70	1.349	137.488	16.343	0.8023	3.5709	1298.95	490.955
1.0000	1299.0	1026.00	1.348	146.365	16.446	0.8048	3.2759	1332.77	479.480

Overall, the comparative analysis clearly demonstrates that molecular geometry plays a crucial role in determining acoustic and thermodynamic behavior. Linear alcohols promote stronger interactions and greater non-ideality than branched alcohols, consistent with previous ultrasonic and thermodynamic studies [26-30].

5. Conclusions

The present ultrasonic and thermophysical study confirms significant composition- and temperature-dependent behavior in ethylbenzoate + alcohol binary mixtures. Stronger molecular interactions and greater deviation from ideality are observed in the ethylbenzoate + 2-butanol system compared to the branched alcohol system. Ultrasonic techniques prove to be reliable tools for probing molecular interactions and structural effects in liquid mixtures.

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