International Journal of Pharma Research & Review, Feb 2014; 3(2):65-78 ISSN: 2278-6074

Research Article

Ultrasonic Investigations of Molecular Interaction in Binary Mixtures of Benzyl Benzoate with Isomers of Butanol

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ABSTRACT

The density and speed of sound have been measured for the systems (Benzyl Benzoate + *n*-butanol, *sec*-butanol, *tert*-butanol) at different molefraction and at different temperatures 308.15K, 313.15K respectively. From these experimental data the excess/ deviation acoustic parameters such as deviation in isentropic compressibility, excess intermolecular free length, excess acoustic impedance and deviation in ultrasonic velocity have been calculated for the binary systems at 308.15 K and 313.15 K temperatures. The calculated excess / deviation functions have been fitted to Redlich-Kister polynomial using multi parametric non- linear regression analysis to estimate the coefficients and standard errors. The variation of these properties with composition and temperature of the binary mixtures have been studied in terms of molecular interactions between unlike molecules of the mixtures. Further, the results are supported by FTIR spectra.

Keywords: Benzyl Benzoate, *n*-butanol, *sec*-butanol, *tert*-butanol, ultrasonic velocity, density, excess / deviation parameters, Redlich-Kister polynomial, intermolecular interaction, FTIR spectra.

Received 25 Sept 2013 Received in revised form 11 Oct 2013 Accepted 14 Oct 2013

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INTRODUCTION

The work on medicinally used chemical compounds requires the attention of the society in all aspects including ultrasonic behavior. Practically, ultrasonic studies are of immense use to study the molecular interactions when these compounds are in binary mixture form with some other liquids - protic /aprotic /polar /non-polar *etc*. Benzyl Benzoate (bb) is a carboxylate ester, which is used as an insect repellent, a medicine for scabies and also used in oily injections. Behavior of benzyl benzoate in many liquids such as aliphatic alkanes, aromatic alkenes, aliphatic alcohols, substituted benzenes, acetates, ketones and DMSO (super solvent) [1-4] has been thoroughly studied ultrasonically.

Alcohols are self-associated organic liquids, used for the synthesis of other organic compounds. They are also widely used as coupling and dispersing agents in the chemical, pharmaceutical and household industries and as carrier and extraction solvents for natural Products. Branching of alkyl group attached to the hydroxyl group results in abnormal behavior of alcohols. The interaction of alcohol [s] with organic liquids is interesting due to its acidic nature. The O-H bonds in alcohols are polar and allow the release of the hydrogen atom as proton (H+). The order of acidity in alcohols is: 1°-alcohol> 2°- alcohol > 3°-alcohol. This order is due to +I effect [5].

While the interacting ability of alcohols is well established, no such opinion is suggested from literature with regards to Benzyl Benzoate. Keeping this in view; three binary liquid mixtures *n*-butanol, *sec*-butaol and *tert*-butaol with Benzyl Benzoate were selected to study their molecular interactions through their acoustical behavior at two temperatures

308.15 K and 313.15 K respectively. The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values [6-9]. These excess values of free length, acoustic impedance, deviations in isentropic compressibility and ultrasonic velocity in binary liquid mixture are useful in understanding the solute-solvent interactions.

MATERIALS AND METHODS

The chemicals Benzyl Benzoate (>99%) and *n*-butanol, *sec*-butanol and *tert*-butanol (all of AR grade, 99.5%) are acquired from s.d. fine chemicals. The chemicals Benzyl Benzoate and alkanols are purified by employing the standard methods mentio-ned in literature [10,11] respectively.

The purity of the chemicals is assessed by comparing their measured densities (ρ) and ultrasonic velocities (u) which are in good agreement with literature [12 - 15] values as can be seen in **Table 1**.

Table 1: comparison of experimental values of density (ρ) and ultrasonic speed(u) of pure liquids with the corresponding literature values at 303.15 K and 313.15 K.

Pure Liquid	Temperature (K)	Density (Kg.m^{-3})		Ultrasonic velocity (m. s^{-1})	
		Expt	Litt	Expt	Litt
Benzyl Benzoate	308.15	1114.54	--	1493.30	--
	313.15	1109.77	1109.7[a]	1471.44	1471.4[a]
n-butanol	308.15	796.15	796.2[d]	1209.30	1209.3[b]
	313.15	792.30	792.3[c]	1181.50	1181.5[c]
sec-butanol	308.15	793.22	793.2[d]	1177.10	1177.1[c]
	318.15	791.10	791.1[c]	1159.10	1159.1[c]
tert-butanol	308.15	771.10	771.1[c]	1086.70	1086.7[c]
	313.15	766.91	766.9[c]	1065.61	1065.6[c]

a ->Reference(12) , b->Reference(13) , c->Reference(14) , d->Reference(15)

Job's method of continuous variation is used to prepare the mixtures of required proportions. The prepared mixtures are preserved in well-stoppard conical flasks. After mixing the liquids thoroughly, the flasks are left undisturbed to allow them to attain thermal equilibrium. The ultrasonic velocity (u) in liquid and liquids mixtures have been measured using an ultrasonic interferometer (Mittal type, Model F-81) working at 2 MHz fixed frequency with an accuracy of ± 0.1 ms^{-1}. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature. The density (ρ) of pure liquids and liquid mixtures are determined using pycknometer by relative measurement method with an accuracy of ±0.1Kgm^{-3}.The temperature around the pycknometer is maintained within ±0.1K in an electronically operated constant temperature water bath. All the precautions are taken to minimize the possible experimental errors.

THEORY

The ultrasonic velocity (u) and density (ρ) in pure liquids and liquid mixture of various concentrations have been measured at 308.15K and 313.15K respectively.

Thermodynamic and acoustical parameters such as isentropic compressibility (k_S), inter molecular free length (L_f), acoustic impedance (z), are determined using the observed values of velocity and density and the deviation/excess values of isentropic compressibility($\Delta \boldsymbol{ks}$), free length($L^E f$), acoustic impedance (z^E) and ultrasonic velocity (Δu) are evaluated using the following equations

Isentropic compressibility (k_s):

The speed of sound (u) and the density of the medium (ρ) using Newton and Laplace equations

$$k_s = (1/\rho u^2) \qquad (1)$$

Intermolecular free length (L_f)

The free length (L_f) is the distance between the surfaces of the neighbouring molecules and is given by the equation

$$L_f = K_T\, k_s^{1/2} \qquad (2)$$

Where K_T is the temperature dependent constant.

Acoustic Impedance (z)

The acoustic impedance is the product of the velocity of ultrasound in a medium (u) and its density (ρ) which can be calculated by the relation.

$$z = u\rho \qquad (3)$$

where u and are velocity and density of the liquid respectively.

Excess / deviation values (Y^E):

In order to understand the nature of the molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their concentrations, and this has been interpreted to arise from the presence of strong or weak interactions. The difference between the parameters of the real mixtures (Y_{real}) and those corresponding to an ideal mixture($Y_{ideal} = \sum x_i Y_i$) values, namely excess parameters (Y^E) such as free length (L_f^E), acoustic impedance (z^E), and deviations in ultrasonic velocity (Δu), isentropic compressibility (Δk_s), are computed by the relation

$$Y^E = Y_{real} - \sum x_i Y_i \qquad (4)$$

Where $Y^E = L_f^E$, z^E and Δu; x_i is the mole fraction and Y_i is the value of the parameter of the i^{th} component liquid of mixture.

The deviations in isentropic compressibility has been calculated from the equation

$$\Delta k_s = k_S - (\phi_1 k_{S1} + \phi_2 k_{S2}) \qquad (5)$$

Since ks is not additive on mole fraction (x_i) but is additive on volume fraction . Hence, such values are calculated using volume fraction

$$\phi_i = \frac{x_i V_i}{\sum x_i V_i} \qquad (6)$$

The excess/deviation properties (Y^E) have been fitted to Redlich-Kister type polynomial equation [16] using

$$Y^E = x(1-x)\sum_{i=0}^{j} A_i(1-2x)^i \qquad (7)$$

Where $Y^E = L_f^E$, z^E, Δu and Δk_s; x is the mole fraction of the solute, A_i are the adjustable parameters of the function; and are determined using the least square method. In the present investigation 'i' values taken from 0 to 4. The corresponding standard deviations $\sigma (Y^E)$ were calculated using the expression.

$$\sigma(Y^E) = \left[\frac{\Sigma\left(Y^E_{exp} - Y^E_{cal}\right)^2}{(m-n)}\right]^{1/2} \qquad (8)$$

Where 'm' is the total number of experimental points and 'n' is the number of coefficients in equation (6). The calculated values of the coefficients A_i along with the standard deviations (σ) for the systems 308.15 K and 313.15 K are given in **Table 4 (A)** and **4 (B)** respectively.

RESULTS AND DISCUSSION

Ultrasonic velocity (u), density (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance(z) and other related excess/deviation thermodynamic parameters Δk_s, L^E_f, z^E and Δu are evaluated for the binary mixture Benzyl Benzoate in *n*-, *sec*-, *tert*-butanols over the whole concentration range at two temperatures 308.15K and 313.15K are presented in **Tables 2 (A, B, C)** and **Tables 3 (A,B,C)**respectively. The R-K coefficients and standard deviation $\sigma(Y^E)$ values for the systems at 308.15 K and 313.15 K are represented in **Tables 4(A, B)**. The excess / deviation values of isentropic compressibility, free length, acoustic impedance and ultrasonic velocity for all the systems at 308.15 K and 313.15 K are plotted in the **Figures 1 to 8**.

Table 2 (A): Ultrasonic velocity (u), densities (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance (z), their excess thermodynamic parameters L^E_f ,z^E and deviations in Δk_s , Δu as a function of mole fraction (x) of Benzyl Benzoate in *n*-butanol (A) at 308.15K

x	ρ (Kg.m^{-3})	u (m.s^{-1})	k_s(x10^{-10}) (P.a $^{-1}$)	L_f(x10^{-10}) (m)	z(x10^6) (Kg.m^2.s^{-1})	Δk_s(x10^{-10}) (P.a^{-1})	L^E_f(x10^{-10}) (m)	z^E(x10^6) (Kg.m^2.s^{-1})	Δu (m.s^{-1})
1.0000	1114.54	1493.26	4.0238	0.4201	0.1664	0.0000	0.0000	0.0000	0.00
0.9234	1100.00	1475.05	4.1782	0.4281	0.1623	-0.1867	-0.0068	0.0013	3.54
0.8854	1093.26	1470.31	4.2312	0.4308	0.1607	-0.3067	-0.0115	0.0023	9.59
0.7631	1070.76	1450.98	4.4359	0.4411	0.1554	-0.6631	-0.0249	0.0056	24.99
0.6688	1051.13	1433.15	4.6319	0.4507	0.1506	-0.8999	-0.0336	0.0074	33.93
0.5914	1033.61	1416.33	4.8230	0.4599	0.1464	-1.0645	-0.0393	0.0086	39.09
0.4753	1004.38	1385.87	5.1839	0.4768	0.1392	-1.2382	-0.0449	0.0096	41.60
0.3270	959.39	1343.28	5.7766	0.5034	0.1289	-1.3267	-0.0471	0.0097	41.12
0.2768	941.29	1327.51	6.0284	0.5142	0.1250	-1.3045	-0.046	0.0093	39.60
0.1400	881.16	1278.08	6.9475	0.5520	0.1126	-1.0068	-0.0347	0.0065	29.02
0.0000	796.10	1209.30	8.5894	0.6138	0.0963	0.0000	0.0000	0.0000	0.00

Table2 (B): Ultrasonic velocity (u), densities (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance (z), their excess thermodynamic parameters L^E_f ,z^E and deviations in Δk_s , Δu as a function of mole fraction (x) of Benzyl Benzoate in *sec*-butanol (B) at 308.15K

x	ρ (Kg.m^{-3})	u (m.s^{-1})	k_s(x10^{-10}) (P.a $^{-1}$)	L_f(x10^{-10}) (m)	z(x10^6) (Kg.m^2.s^{-1})	Δk_s(x10^{-10}) (P.a^{-1})	L^E_f(x10^{-10}) (m)	z^E(x10^6) (Kg.m^2.s^{-1})	Δu (m.s^{-1})
1.0000	1114.54	1493.26	4.0238	0.4201	0.1664	0.0000	0.0000	0.0000	0.00
0.9243	1100.00	1474.46	4.1816	0.4283	0.1622	-0.2167	-0.0078	0.0013	5.13
0.8868	1092.95	1469.10	4.2393	0.4312	0.1606	-0.3473	-0.0129	0.0025	11.62
0.7361	1063.83	1440.11	4.5325	0.4459	0.1532	-0.8204	-0.0300	0.0061	30.28
0.6787	1053.54	1428.48	4.6516	0.4517	0.1505	-1.0008	-0.0364	0.0076	36.80
0.5906	1032.50	1407.84	4.8866	0.4630	0.1454	-1.2129	-0.0437	0.0089	44.01
0.4689	1002.73	1373.85	5.2837	0.4814	0.1378	-1.4420	-0.0511	0.0102	48.50
0.3293	959.12	1328.91	5.9039	0.5089	0.1275	-1.5323	-0.0531	0.0101	47.69
0.2797	939.97	1311.60	6.1842	0.5208	0.1233	-1.5017	-0.0517	0.0095	46.07
0.1404	880.32	1256.31	7.1972	0.5619	0.1106	-1.1941	-0.0401	0.0070	34.82
0.0000	793.21	1177.10	9.0988	0.6317	0.0934	0.0000	0.0000	0.0000	0.00

Table2 (C): Ultrasonic velocity (u), densities (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance (z), their excess thermodynamic parameters L^E_f , z^E and deviations in Δk_s, Δu as a function of mole fraction (x) of Benzyl Benzoate in *tert*-butanol (C) at 308.15K

x	ρ (Kg.m^{-3})	u (m.s^{-1})	k_s(x10^{-10}) (P.a $^{-1}$)	L_f(x10^{-10}) (m)	z(x10^6) (Kg.m^2.s^{-1})	Δk_s(x10^{-10}) (P.a^{-1})	L^E_f(x10^{-10}) (m)	z^E(x10^6) (Kg.m^2.s^{-1})	Δu (m.s^{-1})
1.0000	1114.54	1493.26	4.0238	0.4201	0.1664	0.0000	0.0000	0.0000	0.00
0.9231	1098.84	1469.63	4.2136	0.4299	0.1615	-0.3334	-0.0113	0.0015	7.63
0.8896	1094.43	1460.24	4.2851	0.4335	0.1598	-0.5069	-0.0168	0.0025	11.86

0.7356	1058.74	1426.53	4.6414	0.4512	0.1510	-1.2068	-0.0413	0.0064	40.76
0.6815	1049.07	1414.30	4.7655	0.4572	0.1484	-1.4737	-0.0501	0.0083	50.52
0.5997	1028.44	1387.82	5.0484	0.4706	0.1427	-1.7620	-0.0591	0.0094	57.30
0.4619	991.41	1334.96	5.6599	0.4982	0.1323	-2.1205	-0.0693	0.0103	60.46
0.3312	949.79	1278.79	6.4383	0.5314	0.1215	-2.2591	-0.0719	0.0103	57.43
0.2795	928.73	1254.43	6.8425	0.5478	0.1165	-2.2119	-0.0696	0.0096	54.09
0.1433	871.31	1181.60	8.2203	0.6005	0.1030	-1.7810	-0.0543	0.0074	36.64
0.0000	771.10	1086.70	10.9817	0.6940	0.0838	0.0000	0.0000	0.0000	0.00

Table3 (A): Ultrasonic velocity (*u*), densities (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance (z), their excess thermodynamic parameters $L^E{}_f$,z^E and deviations in Δk_s ,Δ*u* as a function of mole fraction (x) of Benzyl Benzoate in *n*-butanol (A) at 313.15K

x	ρ (Kg.m^{-3})	*u* (m.s^{-1})	k_s(x10^{-10}) (P.a $^{-1}$)	L_f(x10^{-10}) (m)	z(x10^6) (Kg.m^2.s^{-1})	Δk_s(x10^{-10}) (P.a^{-1})	$L^E{}_f$ (x10^{-10}) (m)	z^E(x10^6) (Kg.m^2.s^{-1})	Δ*u* (m.s^{-1})
1.0000	1109.77	1471.44	4.1618	0.4311	0.1633	0.0000	0.0000	0.0000	0.00
0.9234	1091.35	1454.95	4.3285	0.4396	0.1588	-0.1812	-0.0071	0.0008	5.71
0.8854	1082.94	1449.67	4.3940	0.4429	0.1570	-0.2943	-0.0116	0.0017	11.45
0.7631	1066.08	1426.74	4.6081	0.4536	0.1521	-0.7029	-0.0259	0.0053	23.98
0.6688	1046.11	1409.67	4.8105	0.4635	0.1475	-0.9616	-0.0353	0.0073	34.25
0.5914	1028.88	1396.44	4.9841	0.4717	0.1437	-1.1696	-0.0429	0.0089	43.46
0.4753	1000.28	1370.59	5.3219	0.4875	0.1371	-1.4047	-0.0508	0.0104	51.28
0.3270	951.57	1326.66	5.9709	0.5163	0.1262	-1.4770	-0.0523	0.0098	50.34
0.2768	931.40	1309.36	6.2625	0.5288	0.1220	-1.4284	-0.0500	0.0091	47.60
0.1400	870.88	1256.40	7.2742	0.5699	0.1094	-1.0837	-0.0369	0.0060	34.30
0.0000	792.30	1181.50	9.0416	0.6354	0.0936	0.0000	0.0000	0.0000	0.00

Table3 (B): Ultrasonic velocity (*u*), densities (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance (z), their excess thermodynamic parameters $L^E{}_f$,z^E and deviations in Δk_s , Δ*u* as a function of mole fraction (x) of Benzyl Benzoate in *sec*-butanol (B) at 313.15K

x	ρ (Kg.m^{-3})	*u* (m.s^{-1})	k_s(x10^{-10}) (P.a $^{-1}$)	L_f(x10^{-10}) (m)	z(x10^6) (Kg.m^2.s^{-1})	Δk_s(x10^{-10}) (P.a^{-1})	$L^E{}_f$ (x10^{-10}) (m)	z^E(x10^6) (Kg.m^2.s^{-1})	Δ*u* (m.s^{-1})
1.0000	1109.77	1471.44	4.1618	0.4311	0.1633	0.0000	0.0000	0.0000	0.00
0.9243	1092.72	1455.92	4.3173	0.4391	0.1591	-0.2196	-0.0084	0.0012	8.12
0.8868	1085.29	1448.46	4.3918	0.4428	0.1572	-0.3382	-0.0129	0.0020	12.37
0.7361	1063.37	1421.19	4.6560	0.4560	0.1511	-0.8941	-0.0324	0.0067	32.17
0.6787	1052.07	1411.25	4.7725	0.4616	0.1485	-1.0824	-0.0392	0.0082	40.16
0.5906	1032.93	1394.00	4.9820	0.4716	0.1440	-1.3394	-0.0483	0.0100	50.43
0.4689	997.51	1361.68	5.4067	0.4913	0.1358	-1.5448	-0.0550	0.0105	56.12
0.3293	950.79	1317.46	6.0596	0.5202	0.1253	-1.6212	-0.0564	0.0100	55.50
0.2797	931.65	1299.78	6.3534	0.5326	0.1211	-1.5871	-0.0548	0.0094	53.31
0.1404	866.92	1243.00	7.4658	0.5774	0.1078	-1.2030	-0.0402	0.0060	40.04
0.0000	791.10	1159.10	9.4086	0.6481	0.0917	0.0000	0.0000	0.0000	0.00

Table3 (C): Ultrasonic velocity (u), densities (ρ), isentropic compressibility(k_s), intermolecular free length(L_f), acoustic impedance (z), their excess thermodynamic parameters L^E_f, z^E and deviations in Δk_s, Δu as a function of mole fraction (x) of Benzyl Benzoate in *tert*-butanol (C) at 313.15K

x	ρ ($Kg.m^{-3}$)	u ($m.s^{-1}$)	$k_s(x10^{-10})$ ($P.a^{-1}$)	$L_f(x10^{-10})$ (m)	$z(x10^6)$ ($Kg.m^2.s^{-1}$)	$\Delta k_s(x10^{-10})$ ($P.a^{-1}$)	L^E_f($x10^{-10}$) (m)	$z^E(x10^6)$ ($Kg.m^2.s^{-1}$)	Δu ($m.s^{-1}$)
1.0000	1109.77	1471.44	4.1618	0.4311	0.1633	0.0000	0.0000	0.0000	0.00
0.9231	1095.99	1450.64	4.3358	0.4400	0.1590	-0.3876	-0.0130	0.0020	10.40
0.8896	1090.05	1442.35	4.4097	0.4437	0.1572	-0.5619	-0.0189	0.0029	15.71
0.7356	1061.68	1402.42	4.7891	0.4624	0.1489	-1.3305	-0.0441	0.0072	38.28
0.6815	1050.65	1391.57	4.9151	0.4685	0.1462	-1.6072	-0.0534	0.0089	49.39
0.5997	1032.33	1370.27	5.1590	0.4799	0.1415	-1.9710	-0.0653	0.0109	61.28
0.4619	994.73	1322.66	5.7464	0.5065	0.1316	-2.3947	-0.0780	0.0122	69.60
0.3312	947.12	1265.53	6.5925	0.5425	0.1199	-2.4924	-0.0792	0.0112	65.51
0.2795	927.14	1239.90	7.0159	0.5597	0.1150	-2.4453	-0.0767	0.0105	60.86
0.1433	858.96	1167.22	8.5452	0.6177	0.1003	-1.8972	-0.0576	0.0069	43.46
0.0000	766.90	1065.60	11.4835	0.7161	0.0817	0.0000	0.0000	0.0000	0.00

Table 4 (A): R-K coefficients (A_i) and standard deviation σ(Y_i) for the systems at 308.15 K

property	system	A_0	A_1	A_2	A_3	A_4	σ(Y_i)
	bb+*n*-butanol	-4.8254	-2.5767	-1.7982	-1.7205	0.1412	0.0065
$\Delta k_s(x10^{-10})$	bb+*sec*-butanol	-5.5567	-3.1832	-1.7370	-1.3815	-0.0742	0.0288
($P.a^{-1}$)	bb+*tert*-butanol	-8.1460	-4.4556	-2.5529	-3.1175	-1.0658	0.1904
	bb+*n*-butanol	-1.7590	-0.8369	-0.5966	-0.6043	0.2260	0.4090
$L^E_f(x10^{-10})$	bb+*sec*-butanol	-1.9861	-1.0211	-0.4793	-0.4550	0.0563	0.0451
(m)	bb+*tert*-butanol	0.4130	0.1060	0.0183	0.2022	-0.0117	1.3589
	bb+*n*-butanol	0.3770	0.1356	0.1181	0.1036	-0.203	0.0829
$z^E(x10^6)$	bb+*sec*-butanol	0.3961	0.1610	0.0321	0.0227	-0.1418	0.0039
($Kg.m^2.s^{-1}$)	bb+*tert*-butanol	0.4130	0.1060	0.0183	0.2022	-0.0117	0.0024
	bb+*n*-butanol	1.6554	0.3429	0.5425	1.1144	-0.940	0.0057
Δu	bb+*sec*-butanol	1.9119	0.5589	0.2118	1.0368	-0.1854	0.0085
($m.s^{-1}$)	bb+*tert*-butanol	2.4399	0.0890	-0.1000	2.6065	0.5219	0.0284

Table 4 (B): R-K coefficients (A_i) and standard deviation σ(Y_i) for the systems at 313.15 K

property	system	A_0	A_1	A_2	A_3	A_4	σ(Y_i)
	bb+*n*-butanol	-5.4303	-3.4261	-1.1432	0.2532	1.0514	0.0444
$\Delta k_s(x10^{-10})$	bb+*sec*-butanol	-6.0118	-3.0751	-1.0003	-2.9192	-2.1137	0.0196
($P.a^{-1}$)	bb+*tert*-butanol	-9.0654	-5.2094	-1.2822	-3.1258	-3.6439	0.0072
	bb+*n*-butanol	-1.9733	-1.1512	-0.2310	0.2692	0.5695	0.0845
$L^E_f(x10^{-10})$	bb+*sec*-butanol	-2.1596	-0.9316	-0.1187	-1.1685	-0.8805	0.0109
(m)	bb+*tert*-butanol	-3.0205	-1.4786	0.0688	-1.0606	-1.5308	0.0069
	bb+*n*-butanol	0.4024	0.1985	-0.0302	-0.2065	-0.4349	0.0083
$z^E(x10^6)$	bb+*sec*-butanol	0.4249	0.0508	-0.1089	0.3983	0.2011	0.0054
(Kg. $m^2.s^{-1}$)	bb+*tert*-butanol	0.6623	-3.405	3.5160	10.0637	-0.7305	0.2526
	bb+*n*-butanol	1.9986	1.1019	-0.5458	-0.2652	0.2269	0.0200
Δu	bb+*sec*-butanol	2.2278	0.7037	-0.6489	1.8708	2.2139	0.0183
($m.s^{-1}$)	bb+*tert*-butanol	2.7704	0.7510	-1.7360	1.7101	3.2789	0.0188

Fig(1). Mole fraction with deviation in isentropic compressibility at 308.15K

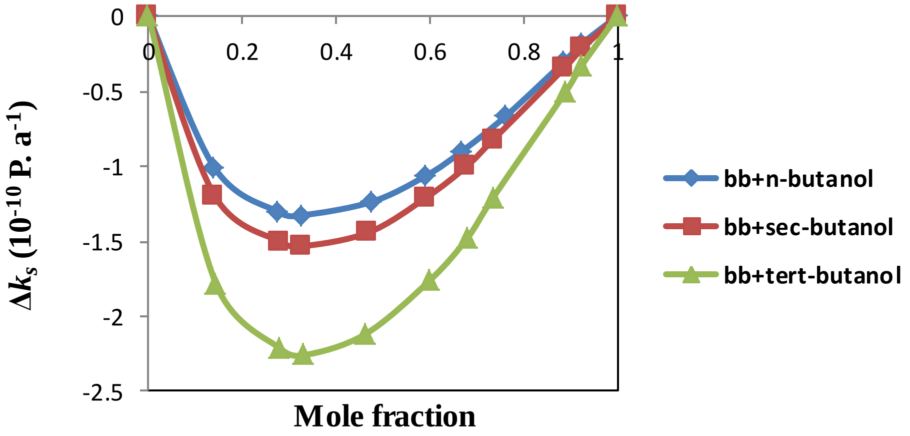


Fig (2). Mole fraction with deviation in isentropic compressibility at 313.15 K

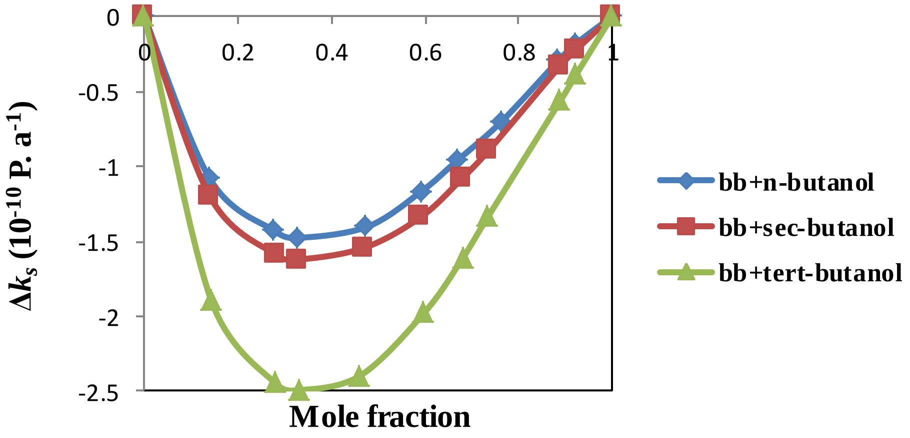


Fig (3). Mole fraction with excess free length at 308.15 K

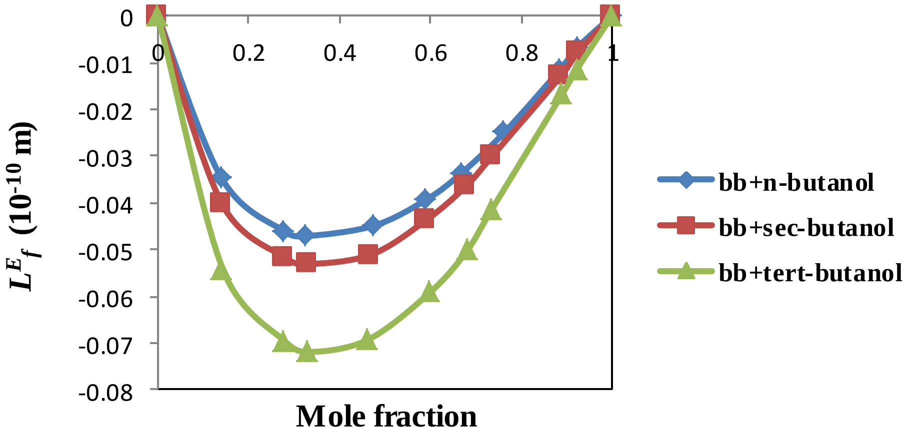


Fig (4). Mole fraction with excess free length at 313.15 K

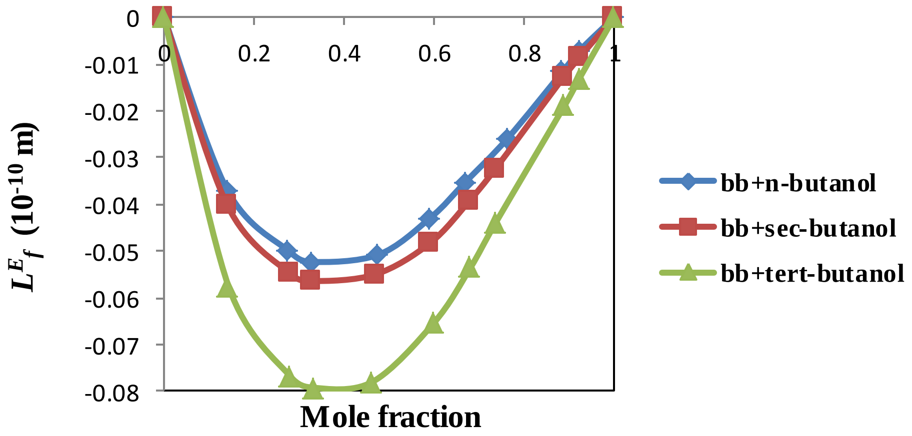


Fig (5). Mole fraction with excess acoustic impedence at 308.15 K

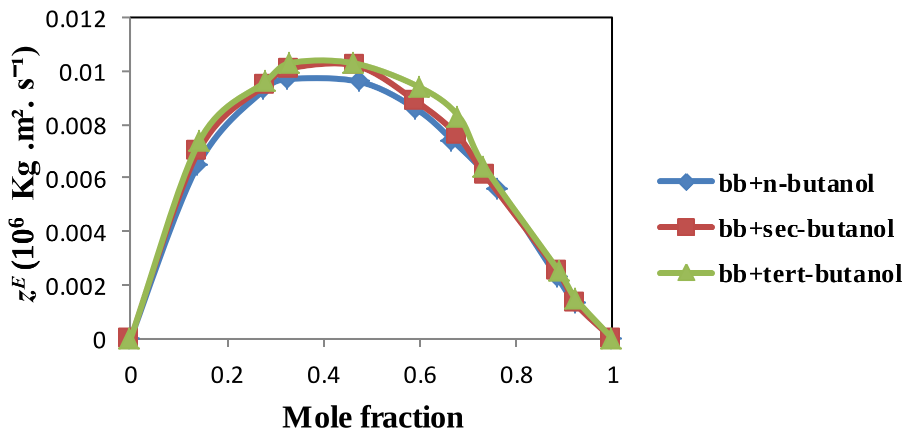
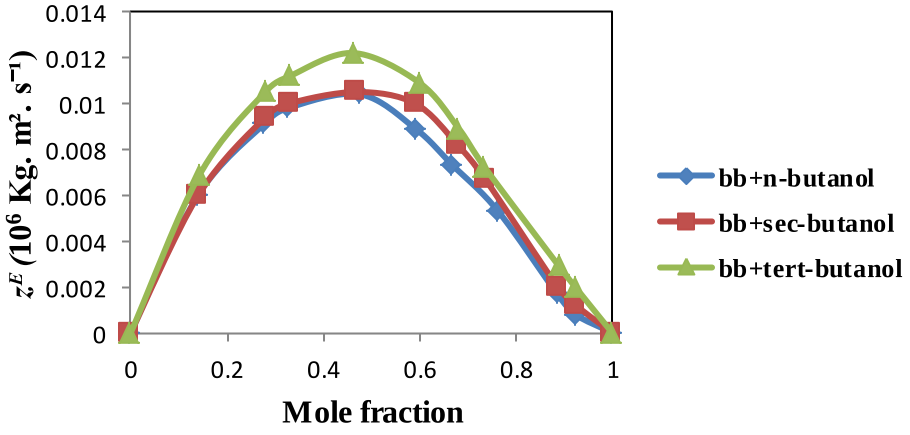


Fig (6). Mole fraction with excess acoustic impedence at 313.15 K



Fig(7).Mole fraction with deviation in ultrasonic velocity at 308.15 K

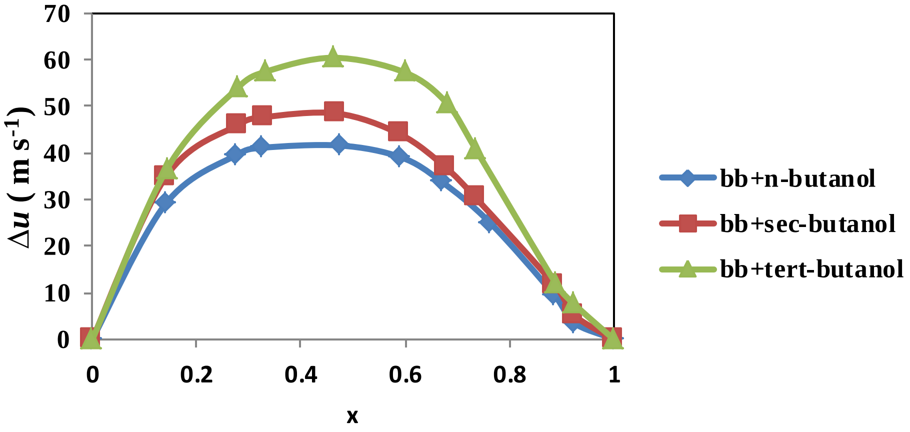
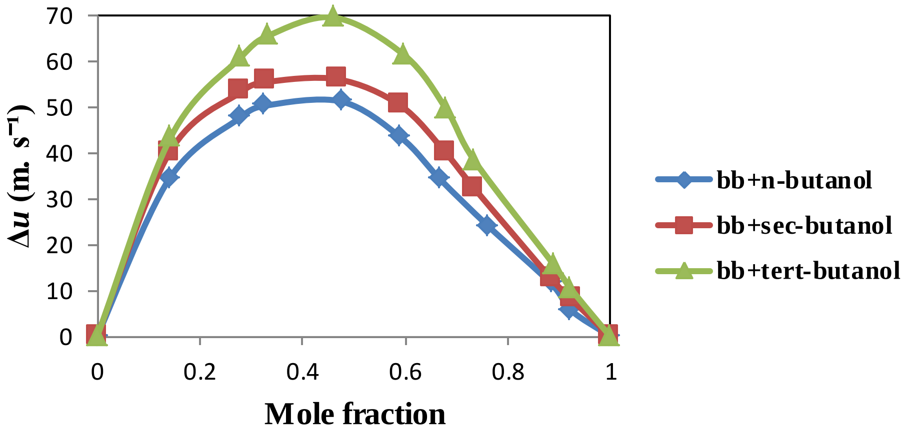
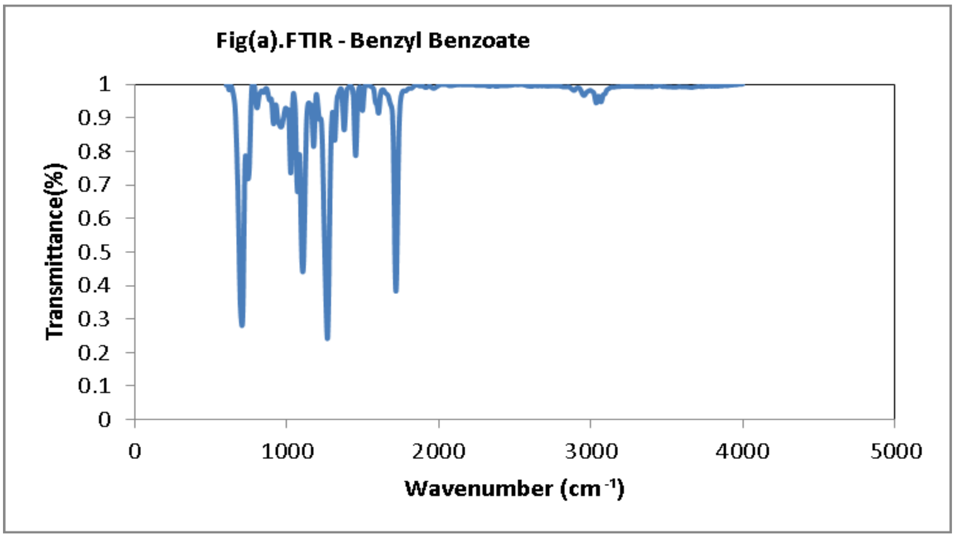


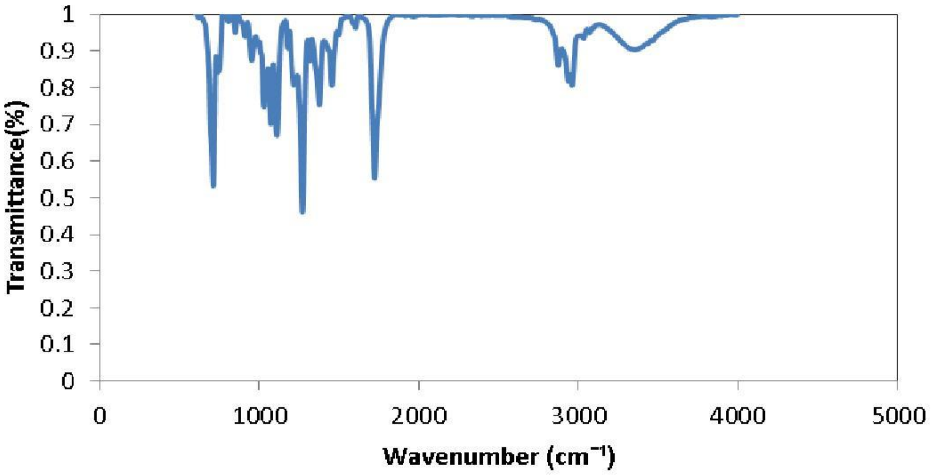
Fig (8). Mole fraction with deviation in ultrasonic velocity at 313.15 K



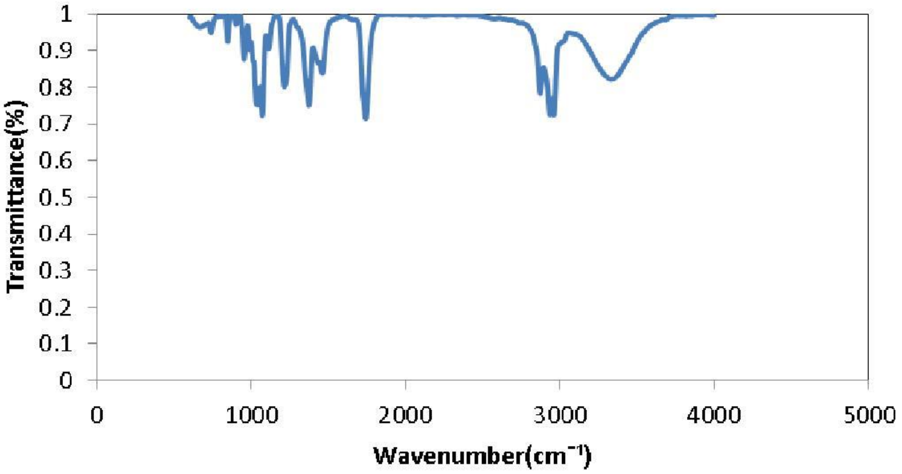


Fig(a).FTIR - Benzyl Benzoate

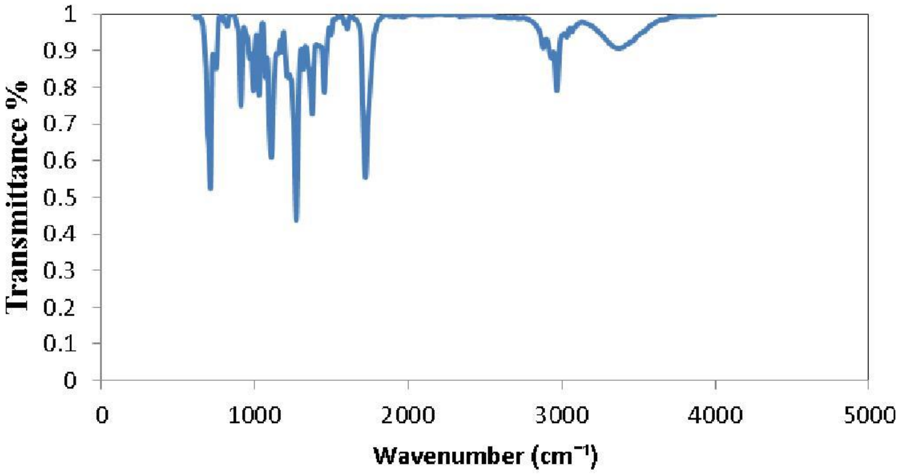
Fig(b).FTIR - BB(5)+n-Butanol(5)

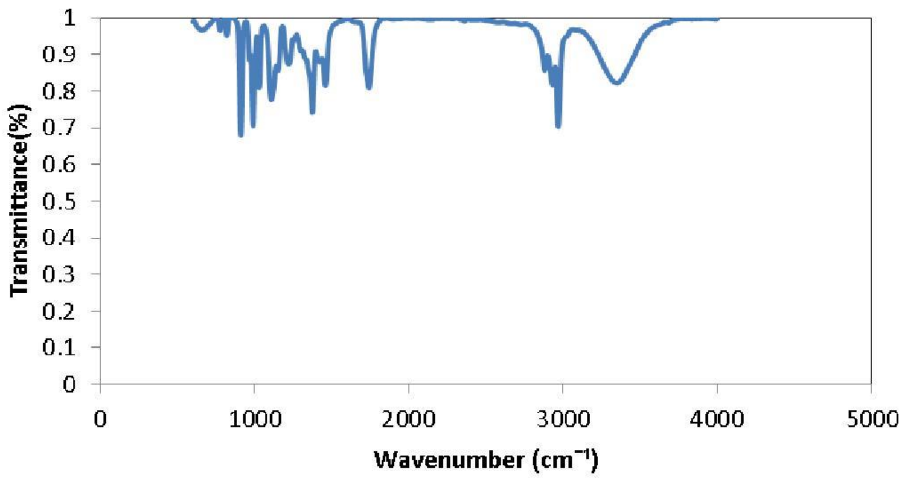


Fig(c).FTIR - n-Butanol

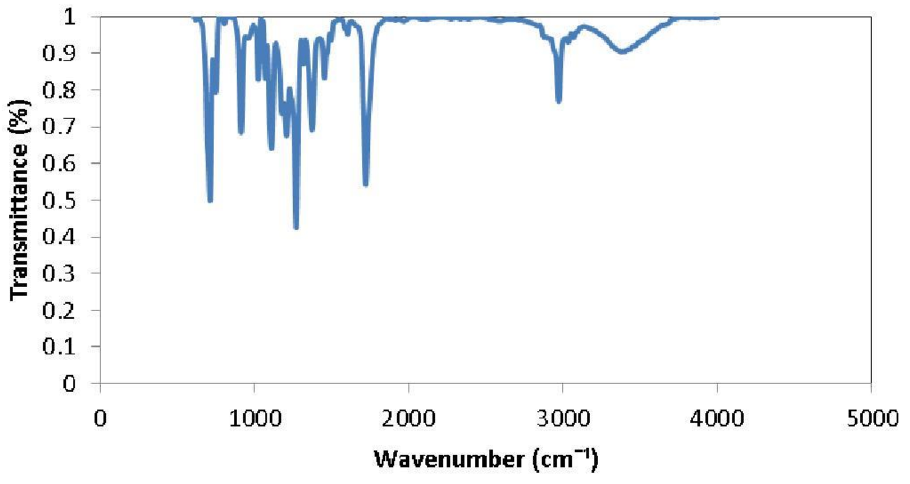


Fig(d).FTIR - BB(5)+sec-Butanol(5)

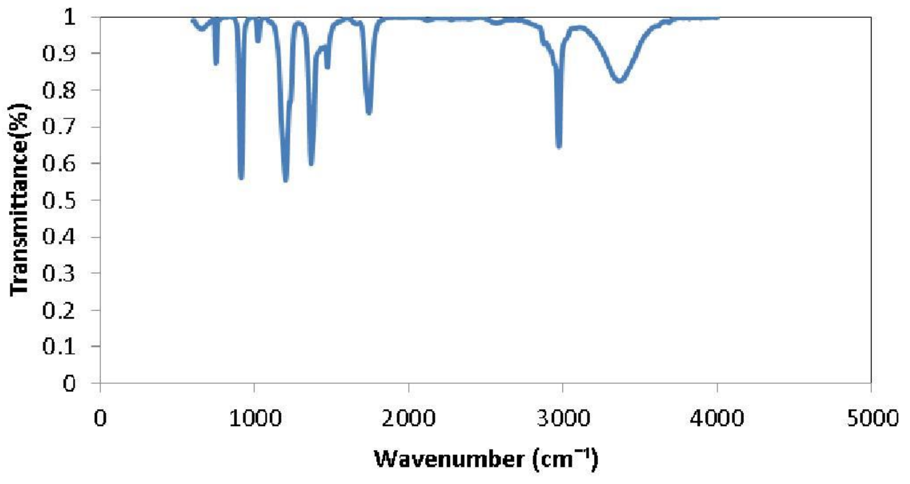




Fig(e).FTIR - sec-Butanol



Fig(f).FTIR - BB(5)+tert-Butanol(5)



Fig(g).FTIR - tert-Butanol

The non-linear variation of excess/deviation properties with mole fraction of Benzyl Benzoate is responsible for non-ideality in the systems of binary liquid mixture [17]. The factors responsible for such departure from ideality may either be due to the presence of intermolecular forces between the constituents in the mixture, or to compound formation between solute and solvent, or as a result of association of either to form complex molecules [18]. These excess/ deviation parameters throw light upon the strength of interaction, and their variation with mole fraction finds application in characterizing the physico-chemical behaviour of liquid mixtures [19].

From the **Tables 2(A, B, C)** and **3(A, B, C)**, the deviation in isentropic compressibility (Δk_s) and excess free length ($L^E{}_f$) are negative. The curves highlighted in **Figures 1 to 4** shows that both Δk_s and $L^E{}_f$ curves are negative for all the systems under investigation. The nature of Δk_s and $L^E{}_f$ play vital role in assessing the compactness due to molecular rearrangement. The extent of molecular interactions in liquid mixtures may be due to charge transfer, dipole-induced-dipole, dipole-dipole interactions and interstitial accommodation, leading to more compact structure giving Δk_s and $L_f{}^E$ negative. The values of the excess/ deviation functions Δk_s, $L^E{}_f$ depend upon several physical and/or chemical contributions. The physical contribution consists of dispersion forces or weak dipole-dipole interaction that leads to positive values Δk_s and $L^E{}_f$. Another factor, which involves a physical contribution, is the geometrical effect allowing the fitting of molecules of two different sizes into each other's structure resulting in negative Δk_s and $L^E{}_f$ values. The strength of the interactions increases with temperatures as observed from more negative values of the excess parameters. They are negative throughout and become more negative at all concentrations as the temperature is increased.

In hetero-molecular interaction between the component molecules of the mixtures, Fort and Moore [20] found that the negative value of deviation in isentropic compressibility indicates greater interaction between the components of the mixtures due to the formation of hydrogen bond. Thus the negative Δk_s values for binary mixtures indicate strong interactions between Benzyl Benzoate and the three isomers of butanols. It is also evident from the tables that the negative values of Δk_s are in the increasing order for all the existing systems which implies that the interactions are in the order: bb+*tert*-butanol>bb+*sec*-butanol>bb+*n*-butanol.

According to Ramamoorthy and Alwan [21], negative values of excess intermolecular free length $L^E{}_f$ indicates that sound waves cover longer distances due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort and Moore[20] indicated that the positive values of excess free length should be attributed to the dispersive forces, and negative excess values should be due to hydrogen bond formation between solute and solvent. In the present study the negative contribution in all the systems prevail to the existence of greater interactions. Spencer , Jeffery and Robert [22] have also reported a similar observation on the basis of excess values of free length. It is also evident from the tables that negative values of $L^E{}_f$ are in the increasing order which implies that these interactions are in the order: bb + *tert*-butanol > bb+*sec*-butanol > bb+*n*-butanol.

From the **Tables 2 (A, B, C)** and **3(A, B, C)**, the excess values of z^E are found to be positive and the curves highlighted in **Figures (5, 6)** show the same for all the systems under investigation. In another words, the curve of z^E in Figures shows the opposite trends as observed in **Figures (1, 2, 3, and 4**) for Δk_s and $L^E{}_f$. According to Ali, Hyder and Nain [23], the nature of the positive values of z^E is attributed to specific interaction between the hetero-molecules. This further supports our earlier finding.

From the **Figures (7) and (8)**, it is observed that the deviation in ultrasonic velocity Δu for all the three binary liquid mixtures is positive over the whole range of mole fraction at all temperatures. According to Ali *et al.* [24], positive deviations in Δu from linear dependence suggest the presence of strong interaction and more positive values means much more strong interactions between the component of molecules. Therefore basing on the above reference for the present scenario, interactions are found to be in the order: bb+*tert*-butanol>bb+*sec*-butanol>bb+*n*-butanol, this again reinforces our view regarding the interaction between **bb** and *n*-butanol, *sec*-butanol, *tert*-butanol mole-cules. Similar trends in Δu have also been reported for dimethylsulphoxide+N, Ndimethylformamide/N,N dimethylacet-amide binary mixtures [25]. Generally in an IR spectrum of absorption, the change in the intensity is related to the interaction between solute and solvent. According to Rajendran [26], large changes in absorption show strong interaction in the system. As per the FTIR **figures (a - g)**, the present mixtures show large variations in their intensity and hence it supports the fact that strong interactions take place in the liquid mixture of Benzyl Benzoate +*n*-butanol, *sec*-butanol, *tert*-butanol.

CONCLUSION

From the present study, it may be concluded that the variation in the acoustic parameters, the sign and extent of deviation of the excess function derived from the ultrasonic velocity and density suggest the presence of molecular interaction between the components of molecules in the binary liquid mixtures. The negative values of Δk_s, L^E_f and the positive values of Z^E, Δu in all the systems at all temperatures reveal the presence of strong interactions between the component molecules in the mixtures. The interaction tends to be stronger with rise in temperature. The existence of strong molecular interaction in the mixture is in the order: bb+*tert*-butanol>bb+*sec*-butanol>bb+*n*-butanol. It is also supported by the IR spectra. The conclusions highlight the importance of ultrasonic method in detecting strong molecular interaction between the component molecules of the mixtures.

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