

# Theoretical Analysis of Ultrasonic Velocities in Binary Liquid Mixtures of Benzylamine with Alicyclic and Aromatic Ethers At 303.15 K

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**ABSTRACT:** Ultrasonic velocities and densities of four binary liquid mixtures of benzyl amine (BA) with four ethers, namely, tetrahydrofuran (THF), 1,4-dioxane (DIOX), anisole (ANI) and diphenyl ether (DPE) were measured experimentally as a function of composition at 303.15 K over the entire concentration range. The theoretical values of ultrasonic velocity were computed using Nomoto's relation ( $u_{\text{NOM}}$ ), Van Dael Vangeel ( $u_{\text{VDV}}$ ) ideal mixing relation, Impedance dependent relation ( $u_{\text{IDR}}$ ), Junjie's theory ( $u_{\text{JUN}}$ ) and Kudriavtsev relation ( $u_{\text{KUD}}$ ). A good agreement is found between experimental and theoretical ultrasonic velocities.  $u_{\text{exp}}^2/u_{\text{the}}^2$  has also been evaluated for non – ideality in the mixtures. The relative applicability of these theories to the present systems has been checked and discussed. The results are explained in terms of intermolecular interactions occurring in these binary systems.

**KEYWORDS:** Theoretical analysis, Ultrasonic velocity, liquid mixture, Benzyl amine- ethers, non – ideal.

## I. INTRODUCTION

Ultrasonic study of liquids and liquid mixtures has gained much importance in assessing the nature of molecular interactions and also helpful in investigating the physico-chemical behavior of such system. The increasing use of THF, DIOX, aromatic ethers and aromatic amines in many industrial processes created theoretical interest in understanding the nature of associated solutions. These studies have greatly stimulated the need for extensive information on properties of mixtures involving these components. Different volumetric and thermal effects are observed upon mixing because of the molecular interactions between ethers + amine [1–3]. The formation of hydrogen bonds is suggested between primary amino and secondary imino groups with weak proton donor ability and the unshared electron pairs on the oxygen atom of ether. Several researchers [4–8] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of ultrasonic velocities with the theoretical relations of Nomoto [9], Van Dael and Vanjeel [10], Impedance relation [11], Junjie [12], Kudriavtsev relation [13] and interpreted the results in terms of molecular interaction. Since these acoustic parameters provide better insight into molecular environments in liquid mixtures, it seemed important to study molecular interactions in terms of these parameters in binary mixtures. In the present paper, we report the measured values of ultrasonic velocities and densities of four binary liquid mixtures of Benzylamine with tetrahydrofuran, 1,4-dioxane, anisole and diphenylether and various theoretical relations are compared with the experimental values of ultrasonic velocities at 303.15 K.

## II. EXPERIMENTAL DETAILS

All the compounds used in the present work were of AnalaR grade samples and they were purified before use in accordance with the procedure described elsewhere [14]. The estimated purity for the three compounds was > 99.8%. Ultrasonic sound velocities were measured accurately in a single crystal variable path ultrasonic interferometer operating at 2 MHz frequency supplied by Mittal Enterprises, India, Model F81, at 303K with an accuracy of 0.2 m/s. The densities of the solutions were determined using a 10 ml specific gravity bottle and a Shimadzu digital balance of

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accuracy  $\pm 0.1$  mg. Digitally controlled and well-stirred thermostatic water bath with a temperature  $T = (303.15 \pm 0.1)$  K was used for all the measurements.

### III. THEORY

Various theories used for evaluating ultrasonic velocities in binary liquid mixtures and their equations are as follows.

1. **Nomoto** established an empirical relation for ultrasonic velocity in binary liquid mixtures as

$$u_{NOM} = [(x_1 R_1 + x_2 R_2) / (x_1 V_{m1} + x_2 V_{m2})]^3$$

Where  $x_1$  and  $x_2$  are the mole fraction of 1<sup>st</sup> and 2<sup>nd</sup> components of the liquid mixtures and  $V$  is the molar volume and  $R$  is the molar sound velocity.

$$R = V_{m1} u_1^{1/3} + V_{m2} u_2^{1/3}$$

Where  $u$  is the ultrasonic velocity.

2. **Van Dael and Vanjeel** Ideal mixing relation for ultrasonic velocity in binary liquid mixtures as

$$u_{VDV} = [1 / \{M_{eff} [(x_1 / (M_1 u_1^2)) + (x_2 / (M_2 u_2^2))]\}]^{1/2}$$

Where  $M_1$  and  $M_2$  are the molecular weights and  $u_1$  and  $u_2$  are the ultrasonic velocities of the individual component and  $M_{eff}$  is the molecular weight of the mixtures

3. **Impedance** dependent relation for the ultrasonic velocity in the binary liquid mixtures is given as

$$u_{IDR} = [(x_1 Z_1 + x_2 Z_2) / (x_1 \rho_1 + x_2 \rho_2)]$$

Where  $Z_1$  and  $Z_2$  are acoustic impedance and  $\rho_1$  and  $\rho_2$  densities of the binary mixtures.

4. **Junjie's** relation for the ultrasonic velocity of the mixtures in terms of the mole fraction, molecular weight and density of the mixture is given by

$$u_{JUN} = (x_1 V_{m1} + x_2 V_{m2}) / [M_{eff} * \{(x_1 V_{m1} + x_2 V_{m2}) / (x_1 \rho_1 u_1^2 + x_2 \rho_2 u_2^2)\}]^{1/2}$$

5. **Kudriavtsev** relation for the ultrasonic velocity of the mixtures in terms of molecular weight and ultrasonic velocity is given by

$$u_{KUD} = [((x_1 M_1 u_1^2) / M_{eff}) + ((x_2 M_2 u_2^2) / M_{eff})]^{1/2}$$

6. Absolute Percentage Deviation (APD) in ultrasonic velocity between experimental and theoretical values are calculated as

$$APD = [(u_{Exp} - u_{Theo}) / u_{Exp}] * 100$$

7. Average Absolute Percentage Deviation (AAPD) is calculated by taking average of APD values

$$AAPD = APD / n$$

Where  $n$  is the number of binary mixtures.

### IV. RESULTS AND DISCUSSION

Theoretically evaluated values of ultrasonic velocities for the four binary liquid systems at 303.15 K and the percentage deviations between experimental and theoretical ultrasonic velocity values are given in Table 1. The AAPD values for the four binary systems along with the order of applicability of the theories are summarised in Table 2. The plots of  $u_{exp}^2 / u_{the}^2$ , for various theoretically evaluated values for the four binary systems are shown from Figure. 1. Generally, study of thermo-acoustical and excess thermo-acoustical parameters [15, 16] is useful to explain strength of the interactions between the component molecules of liquid mixtures. However, in cases where there is no possibility for the calculation of acoustical and excess acoustical parameters, these theoretical ultrasonic velocity studies play the major role. It can be seen from Table 2 that, the theoretical values of ultrasonic velocity evaluated by various theories show deviations from experimental values. The limitations and approximations incorporated in these theories are responsible for it [17]. It is assumed that all the molecules are spherical in shape, which is not true every time. In Nomoto's theory, it is supposed that the volume does not change on mixing. Therefore, no interaction between the components of liquid mixtures has been taken into account. The assumption for the formation of ideal mixing relation is that the ratio of specific heats of ideal mixtures and the volumes are also equal.

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### TABLES AND PLOTS

**Table 1 – Theoretically Calculated Velocities and Absolute Percentage Deviations (APD) between experimental and theoretical values of ultrasonic velocities in the binary liquid mixtures containing (BA + 4 Ehers) over the entire mole fraction range of BA at 303.15 K**

Mole fraction of BA	$u_{NOM}$	$u_{VDV}$	$u_{IDR}$	$u_{JUN}$	$u_{KUD}$	% $u_{NOM}$	% $u_{VDV}$	% $u_{IDR}$	% $u_{JUN}$	% $u_{KUD}$
<b>BA + THF</b>										
0.0000	1252.2	1252.2	1252.2	1252.2	1252.2	0.000	0.000	0.000	0.000	0.000
0.0768	1279.0	1256.5	1276.4	1277.2	1286.7	0.079	1.838	0.283	0.219	0.524
0.1577	1306.2	1263.2	1301.4	1302.8	1319.6	0.193	3.476	0.557	0.449	0.832
0.2429	1333.7	1272.9	1327.3	1329.1	1350.9	0.313	4.856	0.793	0.660	0.975
0.3330	1361.7	1286.3	1354.1	1356.1	1381.0	0.448	5.956	0.999	0.856	0.964
0.4282	1390.0	1304.3	1381.9	1383.9	1409.7	0.557	6.688	1.135	0.995	0.854
0.5290	1418.7	1328.1	1410.8	1412.5	1437.3	0.601	6.947	1.159	1.034	0.702
0.6360	1447.8	1359.7	1440.7	1442.2	1463.8	0.562	6.615	1.054	0.953	0.536
0.7497	1477.4	1401.7	1471.7	1472.8	1489.3	0.427	5.524	0.806	0.735	0.380
0.8708	1507.3	1458.6	1504.0	1504.6	1513.9	0.173	3.398	0.389	0.352	0.266
1.0000	1537.6	1537.6	1537.6	1537.6	1537.6	0.000	0.000	0.000	0.000	0.000
<b>BA + DIOX</b>										
0.0000	1321.0	1321.0	1321.0	1321.0	1321.0	0.000	0.000	0.000	0.000	0.000
0.0802	1341.7	1330.8	1337.6	1339.5	1343.3	0.128	0.935	0.429	0.291	0.009
0.1640	1362.6	1342.2	1355.1	1358.6	1365.4	0.192	1.687	0.736	0.485	0.014
0.2516	1383.7	1355.2	1373.6	1378.3	1387.4	0.239	2.290	0.965	0.627	0.026
0.3434	1405.0	1370.4	1393.1	1398.7	1409.2	0.283	2.741	1.128	0.732	0.013
0.4396	1426.6	1388.0	1413.7	1419.8	1430.9	0.303	2.999	1.200	0.776	0.002
0.5406	1448.3	1408.6	1435.6	1441.7	1452.4	0.301	3.038	1.179	0.761	0.019
0.6467	1470.3	1432.8	1458.7	1464.3	1473.9	0.270	2.816	1.055	0.678	0.029
0.7584	1492.5	1461.5	1483.4	1487.8	1495.2	0.206	2.280	0.817	0.521	0.026
0.8759	1514.9	1495.9	1509.6	1512.2	1516.5	0.096	1.352	0.448	0.275	0.004
1.0000	1537.6	1537.6	1537.6	1537.6	1537.6	0.000	0.000	0.000	0.000	0.000
<b>BA + ANIS</b>										
0.0000	1385.2	1385.2	1385.2	1385.2	1385.2	0.000	0.000	0.000	0.000	0.000
0.1000	1400.0	1398.5	1400.3	1401.0	1401.1	0.055	0.047	0.079	0.132	0.132
0.2000	1414.8	1412.2	1415.4	1416.8	1416.8	0.109	0.074	0.152	0.244	0.245
0.3000	1429.8	1426.3	1430.6	1432.3	1432.3	0.141	0.102	0.197	0.316	0.317
0.3999	1444.9	1440.8	1445.8	1447.7	1447.7	0.166	0.115	0.229	0.363	0.363
0.4999	1460.1	1455.8	1461.0	1463.0	1463.0	0.170	0.125	0.235	0.372	0.373
0.5999	1475.4	1471.1	1476.3	1478.2	1478.2	0.161	0.126	0.223	0.352	0.352
0.7000	1490.8	1487.0	1491.6	1493.2	1493.2	0.146	0.108	0.199	0.310	0.310
0.8000	1506.3	1503.3	1506.9	1508.1	1508.1	0.111	0.084	0.152	0.234	0.235
0.9000	1521.9	1520.2	1522.2	1522.9	1522.9	0.065	0.047	0.087	0.133	0.133
1.0000	1537.6	1537.6	1537.6	1537.6	1537.6	0.000	0.000	0.000	0.000	0.000
<b>BA + DPE</b>										
0.0000	1464.0	1464.0	1464.0	1464.0	1464.0	0.000	0.000	0.000	0.000	0.000
0.1488	1471.8	1459.1	1474.1	1471.7	1471.5	0.292	0.573	0.452	0.288	0.270
0.2823	1479.5	1459.2	1483.5	1479.3	1478.9	0.460	0.919	0.731	0.451	0.421

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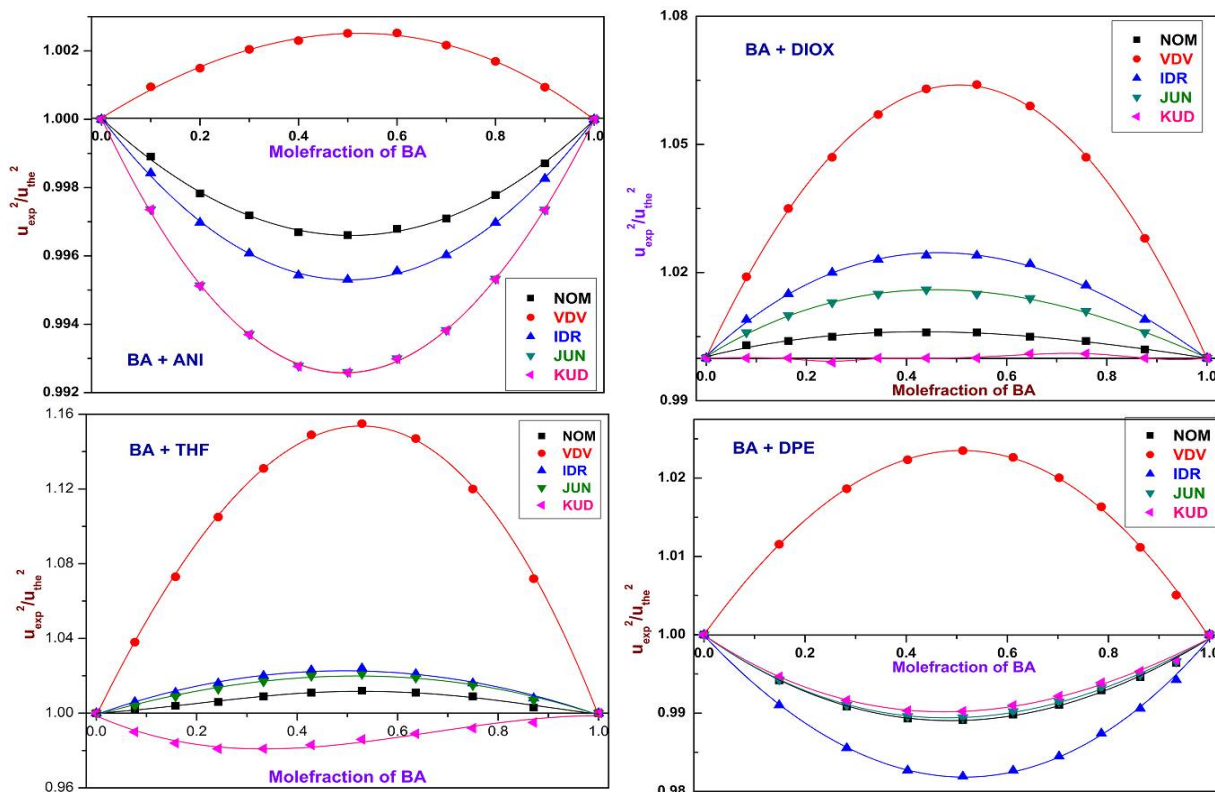
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0.4028	1487.1	1462.9	1492.1	1486.9	1486.3	0.539	1.098	0.877	0.524	0.488
0.5120	1494.6	1469.2	1500.0	1494.3	1493.7	0.550	1.154	0.917	0.531	0.492
0.6114	1502.0	1477.7	1507.4	1501.7	1501.1	0.513	1.113	0.878	0.492	0.454
0.7024	1509.3	1487.7	1514.3	1509.0	1508.4	0.451	0.987	0.785	0.430	0.394
0.7860	1516.5	1498.9	1520.7	1516.2	1515.8	0.357	0.807	0.636	0.337	0.308
0.8629	1523.6	1511.1	1526.7	1523.4	1523.1	0.271	0.554	0.474	0.255	0.234
0.9340	1530.7	1524.0	1532.3	1530.5	1530.3	0.180	0.253	0.289	0.171	0.160
1.0000	1537.6	1537.6	1537.6	1537.6	1537.6	0.000	0.000	0.000	0.000	0.000

**Table 2 – Average Absolute Percentage Deviation (AAPD) for ultrasonic velocities computed by Nomoto, Van Dael & Vanjeel, Impendence Relation, Junjie and Kudriatsev with the order of agreement for each system for four binary systems of Benzylamine with ethers at 303.15 K.**

SYSTEMS	(1) $u_{NOM}$	(2) $u_{VDV}$	(3) $u_{IDR}$	(4) $u_{JUN}$	(5) $u_{KUD}$	ORDER OF AGREEMENT
BA + THF	0.373	5.033	0.797	0.695	0.671	1,5,4,3,2
BA + DIOX	0.224	2.238	0.884	0.572	0.016	5,1,4,3,2
BA + ANI	0.125	0.092	0.173	0.273	0.273	2,1,3,4,5
BA + DPE	0.401	0.829	0.671	0.387	0.358	5,4,1,3,2



**Figure 1 – The variations of ratio of  $u_{exp}^2 / u_{the}^2$  in the binary liquid mixtures containing BA and four ethers over the entire mole fraction range at e 303.15 K**

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Again, no molecular interaction is taken into account. When two liquids are mixed, there is interaction between the molecules of the components. This is due to the presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions [17]. Thus, the observed deviation of theoretical values of ultrasonic velocity from the experimental values shows that the molecular interaction is taking place between the unlike molecules in the liquid mixtures [18].

It is observed from the data in Tables 1 and 2, that in BA + THF system, there is fairly a good agreement between experimental and theoretical values in Nomoto relation followed by Kudriavtsev relation, whereas larger deviations are observed in Van Dael and Vanjeel ideal mixing relation. In the DIOX system, good agreement in Kudriavtsev relation followed by Nomoto relations, whereas higher deviations are observed in Van Dael and Vanjeel ideal mixing relation. In the system of BA and ANIS, there is a good agreement between experimental and theoretical values is observed in Van Dael and Vanjeel ideal mixing relation followed by Nomoto relation and from Table 2 it is observed that similar AAPD values are shown by Junjie and Kudriavtsev relation. In the DPE system, Kudriavtsev's relation shows a good agreement between experimental and theoretical values followed by Junjie's relation and there is no significant deviation between Impedance relation and Van Dael and Vanjeel ideal mixing relation.

It should be noted that Nomoto relation is the modified form of Kudriavtsev relation and hence both the relations show closer deviation in THF and DIOX systems suggests the linearity in molar sound velocity and additivity of molar volume in these systems. These observations suggest that dipole moment and polarizability of the solutes are the two factors which determine strength of interactions and hence the deviation. In the case of THF, being an unsymmetrical cyclic ether has higher dipole moment (1.75D) than the aromatic ethers (ANIS: 1.38D, DPE: 1.3D) and hence there is larger deviation. It may be pointed out here that the symmetric DIOX molecule has comparable polarizability as that of ANIS and DPE. However, the deviation is slightly larger in the BA-DIOX system than the binary systems containing aromatic ethers. This may be due to the fact that DIOX molecule exists in two conformers and there may be conformational changes during interaction with BA. Further, DIOX molecule with two interaction sites (the two ethereal oxygens) may interact with BA stronger than ANIS and DPE. There are reports that Nomoto relation predicting successfully experimental velocity for polar – polar liquid mixtures [19, 20]. These observations are well supported by the plots of  $u_{\text{exp}}^2/u_{\text{the}}^2$  shown in Figure 1. The larger deviations in some intermediate concentration range suggest the existence of strong tendency for the association between component molecules, in this concentration range as a result of hydrogen bonding [21, 22]. These values vary non-linearly with composition suggesting that there is association at some concentration. This is in good agreement with the conclusions drawn by Pandey et al [19] and Kaulgud [20]. The lesser deviation in Van Dael and Vanjeel ideal mixing relation for ANI system may be due to the similar molecular structure of the two components in this mixture. Further the higher polarizability of the two aromatic ethers viz., ANI and DPE show deviations from the alicyclic ether systems.

## V. CONCLUSION

The present investigation on the validity of the theories on ultrasonic velocity for the four binary systems of benzylamine with ethers has been successfully carried out and all the theoretical models fairly predicted ultrasonic velocities reasonably close to the experimental values. The dipole moment and the polarizability of the components play a vital role on the molecular interactions and the computed theoretical velocity depends on the type of interactions involved in these systems.

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