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# Thermo theoretical ultrasonic studies in binary liquid mixtures containing heterocyclic aromatic compound quinoline with 1-butanol at temperatures T= (303.15, 308.15, 313.15 and 318.15) K.

**Sk Fakruddin Babavali[1]*, NT Sarma[2], Ch Srinivasu[3], B Vijay Kumar[1], and K Narendra[1]**

[1]Department of Physics, V.R. Siddhartha Engineering College, Vijayawada (A.P), India.
[2]Department of Physics, Rayalaseema University, Kurnool (A.P), India.
[3]Department of Physics, Andhra Loyola College, Vijayawada (A.P), India.

**ABSTRACT**

Ultrasonic velocities, viscosities and densities in binary liquid mixtures containing heterocyclic aromatic compound quinoline with 1-butanol have been measured at temperatures T=(303.15,308.15,313.15 and 318.15)K over the entire molefraction range of quinoline. Theoretical velocities have been evaluated by using Nomoto ($U_{NOM}$), Impedance ($U_{IMP}$), Van-Dael and Vangeel ($U_{VDV}$), Junjie ($U_{JUN}$) and Rao's specific velocity ($U_{RAO}$) models. Experimentally measured values and theoretical values are compared with each other and a good agreement has been found between them. $U^2_{EXP}$/ $U^2_{IMX}$ has also been evaluated for non-ideality in the liquid mixtures. The results obtained in the comparison are discussed in terms of intermolecular interactions between the component molecules of the binary liquid mixtures.

**Keywords**: Ultrasonic velocity; 1-butanol; quinoline; temperature.

***Corresponding author***

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## INTRODUCTION

Ultrasonic velocity measurement gives valuable information about physicochemical behavior of binary liquid mixtures and also useful in understanding nature of molecular interactions in liquids and liquid mixtures [1-6]. Several researchers [7-9] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results. Ultrasonic velocity measurement data proves to be a very simple and convenient tool to determine various thermodynamic properties of liquid and liquid mixtures. In the present paper the theoretical values of ultrasonic velocity in binary liquid mixtures containing quinoline with 1-butanol at temperatures T=(303.15,308.15,313.15 and 318.15)K over the entire molefraction range of quinoline have been evaluated by using Nomoto [10] , impedance relation [11], Van Dael and Vangeel ideal mix relations [12], Junjie [13] and Rao's Specific velocity relations [14] and are compared with the experimental values. The results are interpreted in terms of molecular interactions between the component molecules of the two binary liquid mixtures and also the non-ideality in the liquid mixtures is explained by the variation of $U^2_{EXP}/U^2_{IMX}$ .

## EXPERIMENTAL SECTION

In the present investigation the chemicals used are of AnalaR grade and are obtained from SDFCL chemicals (quinoline) and MERCK chemicals (1-butanol). The chemicals are purified by standard procedure [15]. The different concentrations of the liquid mixture are prepared by varying mole fractions with respect to Job's method of continuous variation. Stoppard conical flasks are used for preserving the prepared mixtures and the flasks are left undisturbed to attain thermal equilibrium. Ultrasonic pulse echo interferometer (Mittal enterprises, India) is used for ultrasonic velocities measurements and all these measurements are done at a fixed frequency of 3MHz. The temperature of the pure liquids or liquid mixtures is done by using temperature controlled water bath by circulating water around the liquid cell which is present in interferometer. Specific gravity bottle is used for the measurement of densities of pure liquids and liquid mixtures. An electronic weighing balance (Shimadzu AUY220, Japan), with a precision of + or - 0.1 mg is used for the measurements of mass of pure liquids or liquid mixtures. Average of 4 to 5 measurements is taken for each sample. Ostwald's viscometer is used for the measurement of viscosity of pure liquids or liquid mixtures .The time of flow of liquid in the viscometer is measured with an electronic stopwatch with a precision of 0.01s.

## THEORY

Ultrasonic velocities are evaluated in binary liquid mixtures and their equations are as follows [16],

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

$$U_{NOM} = [(X_1R_1+X_2R_2) /(X_1V_1+X_2V_2)]^3 \quad \text{------(1)}$$

Where R is molar sound velocity, $X_1$ and $X_2$ are the mole fractions of 1st and 2nd components of the Liquid mixture and V is molar volume.

**(2). Impedance** dependent relation:

$$U_{IMP} = \Sigma X_iZ_i / \Sigma X_i\rho_i \quad \text{------(2)}$$

Where $X_i$ is the mole fraction, $\rho_i$ the density of the mixture and $Z_i$ is the acoustic impedance.

**(3). Van Dael and Vangeel** Ideal mixing relation:

$$U_{VDV} = [(X_1/M_1U_1^2 + X_2/M_2U_2^2)(X_1M_1+X_2M_2)]^{-1/2} \quad \text{------(3)}$$

Where $M_1$, $M_2$ are molecular weights of constituent components. $U_1$ and $U_2$ are ultrasonic velocities Of individual compounds.

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**(4). Jungie** equation:

$$U_{JUN} = (X_1M_1/\rho_1 + X_2M_2/\rho_2)/[\{X_1M_1+X_2M_2\}^{1/2}\{X_1M_1/\rho_1U_1^2+X_2M_2/\rho_2U_2^2\}]^{1/2} \quad \text{------(4)}$$

Where $\rho_1$ and $\rho_2$ are the densities of constituent components.

**(5). Rao's** specific velocity:

$$U_{RAO} = (\Sigma X_i\, r_i\, \rho_i)^3 \quad \text{------(5)}$$

Where $X_i$ is the mole fraction and $\rho_i$ the density of the mixture. 297

**(6). Percentage deviation** in ultrasonic velocity:

The percentage deviations in ultrasonic velocity between the experimental and theoretical values are calculated as

$$(\Delta U/U)\ \% = ((U_{EXP}-U_{THEORY})/(U_{EXP}))x100 \quad \text{------(6)}$$

## RESULTS AND DISCUSSION

Comparison of experimentally measured values of ultrasonic velocities, densities and viscosities of pure liquids together with the literature values is given in **Table-1**.

**Table 1: The values of ultrasonic velocities (u), densities (ρ) and viscosities (η) of pure liquids along with the literature values at temperature T=303.15K. [17, 18]**

| Liquid | Ultrasonic velocity u(m.s$^{-1}$) | | Density ρ(Kg.m$^{-3}$) | | Viscosity η (m.Pa.S) | |
|---|---|---|---|---|---|---|
| | Exp | Lit | Exp | Lit | Exp | Lit |
| Quinoline | 1553.58 | 1547.00 | 1085.45 | 1085.79 | 2.9320 | 2.9280 |
| 1-butanol | 1222.23 | 1228.00 | 810.00 | 801.07 | 2.2954 | 2.2970 |

The experimental values of ultrasonic velocities along with the theoretically evaluated values by using various theories in the binary liquid mixtures containing quinoline with 1-butanol at temperatures T=(303.15,308.15,313.15 and 318.15)K are given in **Table-2** .The percentage deviations in experimental and theoretical ultrasonic velocity values in the binary liquid mixtures containing quinoline with 1-butanol at temperatures T=(303.15,308.15,313.15 and 318.15)K are given in **Table-3.** The values of $U^2_{EXP}/U^2_{IMX}$ and molecular interaction parameter (α) in the binary liquid mixtures containing quinoline with 1-butanol at temperatures T=(303.15,308.15,313.15 and 318.15)K are given in **Table-4.**

**Table-2: Experimental and theoretical values of ultrasonic velocities in the binary liquid mixtures containing (quinoline + 1-butanol) over entire molefraction range of quinoline at four temperatures T=(303.15,308.15,313.15 and 318.15 )K.**

| (Quinoline + 1-butanol) | | | | | | |
|---|---|---|---|---|---|---|
| Molefraction ($X_1$) | $U_{EXP}$ ms$^{-1}$ | $U_{NOM}$ ms$^{-1}$ | $U_{IMP}$ ms$^{-1}$ | $U_{VDV}$ ms$^{-1}$ | $U_{JUN}$ ms$^{-1}$ | $U_{RAO}$ ms$^{-1}$ |
| T=303.15K | | | | | | |
| 0.0000 | 1222.23 | 1222.23 | 1222.23 | 1222.23 | 1273.23 | 1222.23 |
| 0.0787 | 1255.10 | 1253.02 | 1256.27 | 1239.43 | 1304.89 | 1246.41 |
| 0.1612 | 1287.97 | 1284.32 | 1290.11 | 1258.56 | 1310.17 | 1272.11 |
| 0.2478 | 1320.84 | 1316.13 | 1323.74 | 1279.97 | 1337.52 | 1299.46 |
| 0.3388 | 1353.71 | 1348.47 | 1357.18 | 1304.10 | 1346.65 | 1328.63 |
| 0.4346 | 1386.58 | 1381.33 | 1390.41 | 1331.50 | 1357.82 | 1359.79 |

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|---|---|---|---|---|---|---|
| 0.5355 | 1419.45 | 1414.73 | 1423.45 | 1362.90 | 1392.60 | 1393.14 |
| 0.6420 | 1452.32 | 1448.65 | 1456.30 | 1399.23 | 1408.59 | 1428.93 |
| 0.7546 | 1485.19 | 1483.12 | 1488.95 | 1441.81 | 1449.88 | 1467.40 |
| 0.8737 | 1518.06 | 1518.13 | 1521.41 | 1492.43 | 1471.80 | 1508.87 |
| 1.0000 | 1553.68 | 1553.68 | 1553.68 | 1553.68 | 1553.68 | 1553.68 |
| **T=308.15K** | | | | | | |
| 0.0000 | 1204.76 | 1204.76 | 1204.76 | 1204.76 | 1254.99 | 1204.76 |
| 0.0787 | 1238.88 | 1236.65 | 1240.41 | 1222.98 | 1291.44 | 1229.90 |
| 0.1612 | 1273.00 | 1269.12 | 1275.82 | 1243.20 | 1297.45 | 1256.63 |
| 0.2478 | 1307.12 | 1302.19 | 1311.00 | 1265.77 | 1325.44 | 1285.10 |
| 0.3388 | 1341.24 | 1335.85 | 1345.93 | 1291.13 | 1335.54 | 1315.49 |
| 0.4346 | 1375.36 | 1370.11 | 1380.63 | 1319.86 | 1347.83 | 1347.97 |
| 0.5355 | 1409.48 | 1404.98 | 1415.10 | 1352.68 | 1383.79 | 1382.78 |
| 0.6420 | 1443.60 | 1440.47 | 1449.33 | 1390.56 | 1401.33 | 1420.15 |
| 0.7546 | 1477.72 | 1476.58 | 1483.34 | 1434.84 | 1444.38 | 1460.37 |
| 0.8737 | 1511.84 | 1513.31 | 1517.12 | 1487.33 | 1468.54 | 1503.75 |
| 1.0000 | 1550.68 | 1550.68 | 1550.68 | 1550.68 | 1550.68 | 1550.68 |
| **T=313.15K** | | | | | | |
| 0.0000 | 1189.56 | 1189.56 | 1189.56 | 1189.56 | 1236.34 | 1189.56 |
| 0.0787 | 1224.32 | 1222.11 | 1226.81 | 1208.59 | 1284.17 | 1215.47 |
| 0.1612 | 1259.08 | 1255.34 | 1263.72 | 1229.68 | 1290.12 | 1243.05 |
| 0.2478 | 1293.84 | 1289.28 | 1300.29 | 1253.18 | 1318.07 | 1272.43 |
| 0.3388 | 1328.60 | 1323.92 | 1336.54 | 1279.54 | 1328.36 | 1303.81 |
| 0.4346 | 1363.36 | 1359.29 | 1372.46 | 1309.34 | 1341.02 | 1337.39 |
| 0.5355 | 1398.12 | 1395.39 | 1408.07 | 1343.33 | 1377.45 | 1373.38 |
| 0.6420 | 1432.88 | 1432.24 | 1443.36 | 1382.50 | 1395.83 | 1412.06 |
| 0.7546 | 1467.64 | 1469.84 | 1478.33 | 1428.18 | 1439.96 | 1453.72 |
| 0.8737 | 1502.40 | 1508.22 | 1513.00 | 1482.24 | 1465.69 | 1498.69 |
| 1.0000 | 1547.37 | 1547.37 | 1547.37 | 1547.37 | 1547.37 | 1547.37 |
| **T=318.15K** | | | | | | |
| 0.0000 | 1176.33 | 1176.33 | 1176.33 | 1176.33 | 1215.87 | 1176.33 |
| 0.0787 | 1211.30 | 1208.91 | 1214.90 | 1195.83 | 1282.28 | 1202.68 |
| 0.1612 | 1246.27 | 1242.29 | 1252.98 | 1217.42 | 1287.32 | 1230.73 |
| 0.2478 | 1281.24 | 1276.51 | 1290.58 | 1241.46 | 1314.42 | 1260.65 |
| 0.3388 | 1316.21 | 1311.58 | 1327.70 | 1268.40 | 1324.04 | 1292.60 |
| 0.4346 | 1351.18 | 1347.52 | 1364.37 | 1298.82 | 1336.18 | 1326.80 |
| 0.5355 | 1386.15 | 1384.36 | 1400.58 | 1333.50 | 1372.20 | 1363.49 |
| 0.6420 | 1421.12 | 1422.10 | 1436.35 | 1373.41 | 1390.47 | 1402.93 |
| 0.7546 | 1456.09 | 1460.79 | 1471.67 | 1419.92 | 1434.71 | 1445.43 |
| 0.8737 | 1491.06 | 1500.43 | 1506.57 | 1474.89 | 1461.01 | 1491.33 |
| 1.0000 | 1541.05 | 1541.05 | 1541.05 | 1541.05 | 1541.05 | 1541.05 |

**Table 3: Percentage deviations between experimental and theoretical values of ultrasonic velocities in the binary liquid mixtures containing (quinoline + 1-butanol) over entire molefraction range of quinoline at four temperatures T=(303.15,308.15,313.15 and 318.15 )K.**

| (Quinoline + 1-butanol) | | | | | |
|---|---|---|---|---|---|
| **Molefraction ($X_1$)** | **$\%U_{NOM}$** | **$\%U_{IMP}$** | **$\%U_{VDV}$** | **$\%U_{JUN}$** | **$\%U_{RAO}$** |
| **T=303.15K** | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0787 | -0.1660 | 0.0933 | -1.2487 | 3.9669 | -0.6921 |
| 0.1612 | -0.2836 | 0.1660 | -2.2834 | 1.7234 | -1.2313 |
| 0.2478 | -0.3563 | 0.2198 | -3.0940 | 1.2629 | -1.6184 |
| 0.3388 | -0.3870 | 0.2562 | -3.6645 | -0.5218 | -1.8527 |
| 0.4346 | -0.3783 | 0.2765 | -3.9721 | -2.0745 | -1.9322 |

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|---|---|---|---|---|---|
| 0.5355 | -0.3327 | 0.2821 | -3.9842 | -1.8915 | -1.8532 |
| 0.6420 | -0.2524 | 0.2740 | -3.6553 | -3.0113 | -1.6107 |
| 0.7546 | -0.1394 | 0.2532 | -2.9209 | -2.3776 | -1.1976 |
| 0.8737 | 0.0044 | 0.2207 | -1.6886 | -3.0473 | -0.6053 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **T=308.15K** | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0787 | -0.1800 | 0.1238 | -1.2832 | 4.2429 | -0.7250 |
| 0.1612 | -0.3045 | 0.2219 | -2.3408 | 1.9203 | -1.2860 |
| 0.2478 | -0.3773 | 0.2965 | -3.1634 | 1.4019 | -1.6845 |
| 0.3388 | -0.4020 | 0.3497 | -3.7358 | -0.4252 | -1.9202 |
| 0.4346 | -0.3817 | 0.3831 | -4.0354 | -2.0018 | -1.9913 |
| 0.5355 | -0.3191 | 0.3984 | -4.0300 | -1.8229 | -1.8944 |
| 0.6420 | -0.2170 | 0.3970 | -3.6738 | -2.9279 | -1.6244 |
| 0.7546 | -0.0775 | 0.3803 | -2.9020 | -2.2560 | -1.1743 |
| 0.8737 | 0.0973 | 0.3493 | -1.6214 | -2.8643 | -0.5349 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **T=313.15K** | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0787 | -0.1807 | 0.2031 | -1.2844 | 4.8888 | -0.7226 |
| 0.1612 | -0.2968 | 0.3682 | -2.3351 | 2.4652 | -1.2735 |
| 0.2478 | -0.3526 | 0.4986 | -3.1429 | 1.8724 | -1.6545 |
| 0.3388 | -0.3520 | 0.5976 | -3.6928 | -0.0181 | -1.8656 |
| 0.4346 | -0.2984 | 0.6677 | -3.9624 | -1.6387 | -1.9050 |
| 0.5355 | -0.1950 | 0.7115 | -3.9189 | -1.4782 | -1.7692 |
| 0.6420 | -0.0447 | 0.7311 | -3.5163 | -2.5854 | -1.4529 |
| 0.7546 | 0.1501 | 0.7286 | -2.6887 | -1.8857 | -0.9487 |
| 0.8737 | 0.3871 | 0.7057 | -1.3416 | -2.4435 | -0.2470 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **T=318.15K** | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0787 | -0.1977 | 0.2971 | -1.2768 | 5.8595 | -0.7114 |
| 0.1612 | -0.3191 | 0.5382 | -2.3148 | 3.2940 | -1.2466 |
| 0.2478 | -0.3691 | 0.7287 | -3.1051 | 2.5899 | -1.6074 |
| 0.3388 | -0.3517 | 0.8733 | -3.6327 | 0.5951 | -1.7938 |
| 0.4346 | -0.2706 | 0.9761 | -3.8748 | -1.1100 | -1.8041 |
| 0.5355 | -0.1293 | 1.0410 | -3.7986 | -1.0064 | -1.6347 |
| 0.6420 | 0.0693 | 1.0714 | -3.3572 | -2.1565 | -1.2800 |
| 0.7546 | 0.3226 | 1.0703 | -2.4844 | -1.4683 | -0.7323 |
| 0.8737 | 0.6283 | 1.0404 | -1.0842 | -2.0156 | 0.0183 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

**Table 4: Values of $U^2_{EXP}/U^2_{IMX}$ and molecular interaction parameter (α) in the binary liquid mixture containing (quinoline + 1-butanol) over entire molefraction range of quinoline at four temperatures T=(303.15,308.15,313.15 and 318.15 )K.**

| (Quinoline + 1-butanol) | | | | |
|---|---|---|---|---|
| Molefraction ($X_1$) | $U^2_{EXP}/U^2_{IMX}$ | | | |
| | T=303.15K | T=308.15K | T=313.15K | T=318.15K |
| 0.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 0.0787 | 1.0255 | 1.0262 | 1.0262 | 1.0260 |
| 0.1612 | 1.0473 | 1.0485 | 1.0484 | 1.0480 |
| 0.2478 | 1.0649 | 1.0664 | 1.0659 | 1.0651 |
| 0.3388 | 1.0775 | 1.0791 | 1.0782 | 1.0768 |
| 0.4346 | 1.0844 | 1.0859 | 1.0842 | 1.0822 |

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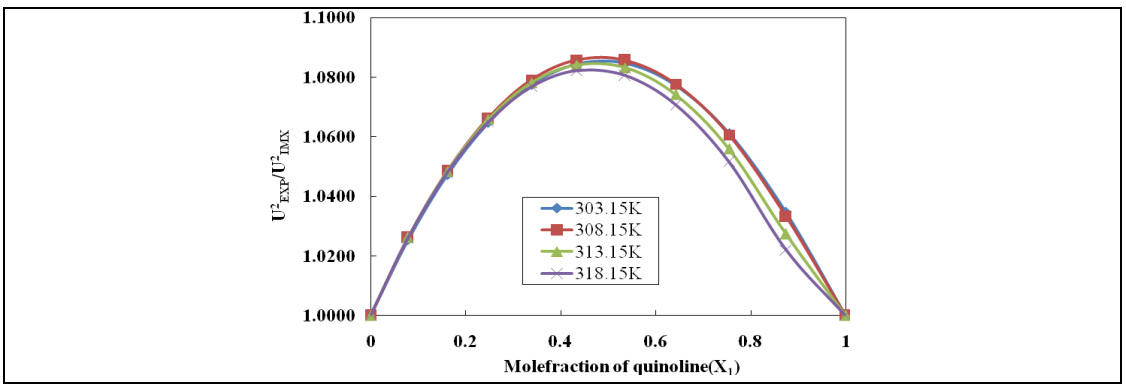
|---|---|---|---|---|
| 0.5355 | 1.0847 | 1.0857 | 1.0832 | 1.0805 |
| 0.6420 | 1.0773 | 1.0777 | 1.0742 | 1.0707 |
| 0.7546 | 1.0611 | 1.0607 | 1.0560 | 1.0516 |
| 0.8737 | 1.0346 | 1.0332 | 1.0274 | 1.0220 |
| 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| **Molefraction ($X_1$)** | **Molecular interaction parameter (α)=( $U^2_{EXP}/U^2_{IMX}$ -1)** | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0787 | 0.0255 | 0.0262 | 0.0262 | 0.0260 |
| 0.1612 | 0.0473 | 0.0485 | 0.0484 | 0.0480 |
| 0.2478 | 0.0649 | 0.0664 | 0.0659 | 0.0651 |
| 0.3388 | 0.0775 | 0.0791 | 0.0782 | 0.0768 |
| 0.4346 | 0.0844 | 0.0859 | 0.0842 | 0.0822 |
| 0.5355 | 0.0847 | 0.0857 | 0.0832 | 0.0805 |
| 0.6420 | 0.0773 | 0.0777 | 0.0742 | 0.0707 |
| 0.7546 | 0.0611 | 0.0607 | 0.0560 | 0.0516 |
| 0.8737 | 0.0346 | 0.0332 | 0.0274 | 0.0220 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

**Table-2** shows the deviation of theoretical values obtained by various theories with experimental values. The limitations and approximations incorporated in these theories and also because of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions [20] interaction between molecules takes place on mixing with each other. These observed deviations of ultrasonic velocity values from the experimental values indicating the existence of molecular interactions between the unlike molecules in the liquid mixtures [21].From **Table-3** shows the negative and positive percentage deviations of the ultrasonic velocity in the binary liquid mixtures. These types of negative and positive percentage deviations indicate the non-ideal behavior of liquid mixtures [21].In such cases the ratio of $U^2_{EXP}/U^2_{IMX}$ is an important tool to measure the non-ideality in liquid mixtures. The outcome of **Table-4** indicates reasonable deviations from ideality, which may be due to the existence of strong dipole-dipole interactions in the liquid mixtures [20-21].

**Fig-1** represent **t**he variations of the ratio of $U^2_{EXP}/U^2_{IMX}$ with the molefraction of quinoline in binary liquid mixtures containing (quinoline + 1-butanol) at temperatures T=(303.15,308.15,313.15 and 318.15)K.

**Fig-1** clearly indicates that ratio of $U^2_{EXP}/U^2_{IMX}$ increases from unity with the increase of molefraction from 0 to 0.5 and above the 0.5 molefraction range the ratio of $U^2_{EXP}/U^2_{IMX}$ decreases and tends to unity at all the observed temperatures in (quinoline + 1-butanol) liquid mixtures. Also the deviation of the ratio $U^2_{EXP}/U^2_{IMX}$ from unity is a direct measure of non-ideality of the system as a consequence of association or other type of interactions which is called as molecular interaction parameter (α). The positive values of α clearly indicate the existence of strong interactions in the liquid mixtures [22].**Table-4** also indicates that, α decreases with the increase of temperature which clearly suggests that interaction becomes weak with the rise of temperature.

**Fig 1: The variations of $U^2_{EXP}/U^2_{IMX}$ in (quinoline + 1-butanol) liquid mixtures at temperatures T=(303.15,308.15,313.15 and 318.15)K .**



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## CONCLUSIONS

Ultrasonic velocities are calculated by using different theories such as Nomoto ($U_{NOM}$), impedance ($U_{IMP}$), Van-Dael and Vangeel ($U_{VDV}$), Junjie ($U_{JUN}$) and Rao's specific velocity ($U_{RAO}$) models and they have been compared with the experimentally measured values at temperatures T=(303.15,308.15,313.15 and 318.15)K. Comparision of these values may be concluded that Nomoto's and Junjie relations have good results. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of molecular interactions in the system studied. Also the positive values of α clearly indicate the existence of strong tendency for the formation of association between the component molecules of the liquid mixtures.

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