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Theoretical Evaluation of Speed of Sound in Binary Liquid Mixtures

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Abstract: *Speeds of sound and densitiesof binary mixturesof 1,4-butanediol (1,4-BD) with methylpyridine isomers (α-picoline and β-picoline) have been measured over the entire range of composition at temperaturesT=(303.15,308.15,313.15 and 318.15)K and at atmospheric pressure.The experimental speeds of sound have been analyzed in terms of relations like Nomoto (U_N), Impedance (U_I), Collision factor theory (U_C), Van-Dael and Vangeel (U_V), Junjie (U_J), Free Length Theory (U_F) and Rao's specific velocity (U_R). A good agreement has been found between experimental and theoretical values. U_{exp}^2/U_{imx}^2 has also been evaluated for non-ideality in the liquid mixtures.Chi-square test for the goodness of the fit is applied to understand the relative applicability of these theories to the present systems. The results were discussed in terms of molecular interactions prevailing in the mixtures.*

Keywords: *speed of sound;binary liquid mixtures;speed of sound models; 1,4-butanediol;picoline.*

1. INTRODUCTION

As a part of our systematic studies on the volumetric and thermodynamic properties of binary mixtures of 1,4-butanediol (1,4-BD) with methylpyridine isomers at different temperatures, in previous paper [1] measurements of densities and speeds of sound have been reported. The molecular interactions in pure and binary liquid mixtures have been studied by measuring speeds of sound by several researchers [2-6]. For predicting and estimating various physico-chemical properties of the systems under consideration, propagation of speed of sound in a medium is a thermodynamic property andhas come to be recognized as a very specific and unique tool. To correlate the molecular structure and macroscopic properties of liquids and for analysis of thermodynamic properties of liquid mixtures some models are important.

1,4-BD is a clear viscous liquid, which is miscible with water and most polar organic solvents. The presence of two hydroxyl groups atvicinal positions (at the positions 1 and 4) of this diol makes it suitable as a useful chemical intermediate in the manufacture of many chemical products.

Picoline refers to three different methylpyridineisomers, all are colourless liquids at room temperature and pressure and are miscible with water and most organic solvents. α-picoline is used as an adhesive for textile tire cord and also a precursor to the agrochemical, nitrapyrin, which prevents loss of ammonia from fertilizers. β-picoline is a useful precursor to agrochemicals, such as chlorpyrifos and used to make antidotes for poisoning by organophosphate acetylcholinesterase inhibitors.

To confirm the earlier conclusions, in this paper we are reportingthe theoretical values of speeds of sound for the two binary systems formed by combination of 1,4-BD with α-picoline andβ-picolineat atmospheric pressure over the entire composition range at 303.15, 308.15, 313.15 and 318.15K evaluated by using Nomoto [7] , impedance relation [8], Collision factor theory [9], Van Deal andVangeel ideal mix relation [10],Junjie [11], Free length theory [12]and Rao's Specific velocity relation [13]and comparing them with the experimental values using Chi-square test. Comparison of theoretical values of speeds of sound with the experimentally measured values in the present binary liquid mixturesis expected to reveal the nature of interactions between the component molecules of the liquid mixtures.The deviation in the variation ofU^2_{exp}/U^2_{imx} fromunity has also been evaluated forexplaining the non-ideality in the liquid mixtures. Of these models, Nomoto's relation and ideal mixing relation were reported to be in good agreement with the experimental results.

2. MATERIALS AND METHODS

1,4-BD and methylpyridine isomers (Sigma-Aldrich, USA, mass fraction purity 0.99) used in this study were purified by standard methods [14,15]. Before use, all chemicals were stored over 0.4nm molecular sieves for 72 hrs to remove the water content, if any, and were degassed at low pressure.The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. All samples were prepared immediately prior to measurements using an electronic balance (CPA-225D, Sartorius, Germany) precisely within $\pm1\times10^{-5}$g. The uncertainty in the mole fraction was estimated to be within $\pm 1\times10^{-4}$.

The densities of the pure liquids and their binary mixtures were measured by using a single-capillary pyconometer (made of Borosil glass) having a bulb capacity of ≈10mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The densities of pure water at the required temperature were taken from the literature [16]. The reproducibility of the density measurements was within $\pm2 \times 10^{-5}$ $g.cm^{-3}$. The temperature of the test liquids during the measurements was maintained to an accuracy of ±0.02K in an electronically controlled thermostatic water bath (Julabo). The speeds of sound in pure liquids and in their binary mixtures were measured using a single-crystal variable-path multifrequency ultrasonic interferometer (Mittal Enterprises, India, Model F-81) operating at 2 MHz. The speeds of sound data were reproducible within ±0.2 m s^{-1}.The reliability of experimental measurements of speed of sound was ascertained by comparing the experimental data of the pure liquids with the corresponding literature values [17, 18] at the studied temperatures.

3. THEORY

Various theories used for evaluating speeds of sound in binary liquid mixtures and their equations are as follows,

Nomoto, assuming the linearity of the molar sound velocity (R) and the additivity of the molar volumes in liquid solution, gave the following relation:

$$U_N = \left(\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right)^3 \quad (1)$$

where R is molar sound velocity, $x_1$and x_2 are the mole fractions of 1st and 2nd components of the liquidmixture and V is molar volume.

Impedancedependent relation: The specific acoustic impedance (Z) of the pure liquids are used for evaluating the speeds of sound in the liquid mixtures by the following relation.

$$U_I = \sum x_i Z_i / \sum x_i \quad (2)$$

Nutsch-Kuhnkies extended the relation given by Schaaffs for predicting speeds of sound in pure liquids on the basis of CFT, for binary liquid mixtures. The relation is:

$$U_m = (U_\infty / V)(x_1S_1 + x_2S_2)(x_1B_1 + x_2B_2) \quad (3)$$

In the equation, S and B are collision factor and actual volume of the molecules per mole respectively of the first and second components respectively and are given by the expressions:

$$S = \frac{UV}{U_\infty B} \text{and} B = \frac{4}{3}\pi r^3 N_0$$

where U_∞ = 1600 m/s, an empirical constant, N_0,the Avogadro number and r is the molecular radius.

Van Dael and Vangeelproposed the following ideal mixing relation for predicting speeds of sound of binary liquid mixtures:

$$U_V = \left[\left(\frac{x_1}{M_1U_1^2} + \frac{x_2}{M_2U_2^2}\right)(x_1M_1 + x_2M_2)\right]^{-1/2} \quad (4)$$

where M_1, M_2 are molecular weights of constituent components. U_1 and U_2 are ultrasonic velocities ofindividual compounds.

The Junjieequation is represented by:

$$U_J = (x_1 V_1 + x_2 V_2)\left[(x_1 M_1 + x_2 M_2)\left[\left(\frac{x_1 M_1}{\rho_1^2 U_1^2}\right) + \left(\frac{x_2 M_2}{\rho_2^2 U_2^2}\right)\right]\right]^{-1/2} \quad (5)$$

Jacobson's intermolecular freelength theory (FLT) is given by:

$$U_F = k / (L_f \rho^{1/2}) \quad (6)$$

where k is Jacobson's constant.

The free length of the mixture L_f is obtained by

$$L_f = (V - \Sigma_i x_i V_{0,i})/\Sigma_i x_i Y_i \quad (7)$$

where $V_{0,i}$ = molar volume of pure component i at 0K, and Y_i = surface area per mole for pure component i. For spherical molecules the surface area per mole of the pure liquid is given by:

$$Y_i = (36\pi N V_{0,i}^{2})^{1/3} \quad (8)$$

The molar volume of pure component i at absolute zero temperature $V_{0,i}$ is obtained by Sugden's formula:

$$V_{i,0} = V_i(1-T/T_{c,i})^{0.3} \quad (9)$$

whereT$_c$ critical temperature.

Rao's specific velocity:

$$U_R = (R/V)^3 \quad (10)$$

where V is the molar volume and R is called Rao's constant or molar sound velocity, which is constant for a liquid at a temperature.

Chi-Square test for goodness of fit:

According to Karl Pearson [19], Chi-square valueis evaluated for the binary liquid mixtures under study using the formula:

$$\chi^2 = \sum_{i=1}^{n}\left(\left(U_{exp} - U_{cal}\right)^2/U_{cal}\right) \quad (11)$$

where n is the number of data points used,U_{exp}, the experimental values of speeds of sound and U_{cal}, the calculated values of speeds of sound

The average percentage deviations (APD) by the different approaches have been computed using the expression:

$$APD = \frac{1}{n}\sum\frac{U_{experimental} - U_{theoretical}}{U_{experimental}} \text{ X } 100\text{----} \quad (12)$$

The degree of intermolecular interaction or molecular association is given by:

$$\alpha = \left[U_{exp}^2 / U_{imx}^2\right] - 1 \quad (13)$$

4. Results and Discussion

The comparison of experimental values of speeds of sound(U) with the literature values are given in Table1. Speeds of sound of two binary liquid mixtures comprising of 1,4-BD with α-picoline or β-picoline have been predicted at 303.15, 308.15, 313.15 and 318.15 K by employing seven approaches viz., Nomoto, Impedance, Van Dael, Junjie, Rao, Collision factory theory and Free length theory models over the entire composition range and are given in Table 2 along with experimental values of speeds of sound. Table 3 records the average percentage deviation (APD) values for all the above mentioned approaches for the two binary mixtures chosen for the present investigation. The variation of U_{exp}^2/U_{imx}^2 with 1,4-BD concentration and temperature is shown in Fig.1 (a,b). The values of Chi-square for the two mixtures and for the seven theories are given in Table 4. Molecular association, α, values at different temperatures are presented in Table 5.

Table1. *Comparison of speeds of sound, U and density, ρ of pure liquids with their literature values at T = 303.15, 308.15, 313.15 and 318.15K*

Compounds	T(K)	U/m.s^{-1}		ρ/kg.m^{-3}	
		Experimental	Literature	Experimental	Literature
1,4 butanediol	303.15	1590.4	1590.1[17]	1009.4	1009.67[17]
	308.15	1580.5	1578.4[17]	1006.8	1006.70[17]
	313.15	1569.2	1566.9[17]	1003.8	1003.73[17]
	318.15	1555.2	1555.4[17]	1000.4	1000.76[17]
α-picoline	303.15	1360.2	1361.0[18]	935.2	935.1[18]
	308.15	1340.4	1339.9[18]	930.3	930.4[18]
	313.15	1320.3	-	925.7	-
	318.15	1300.4	-	920.9	-
β-picoline	303.15	1402.2	1404.1[18]	947.4	947.4[18]
	308.15	1385.0	1384.0[18]	942.7	942.8[18]
	313.15	1365.2	-	938.1	-
	318.15	1345.3	-	934.5	-

Table2. *Experimental and theoretical values of speeds of sound in the binary liquid mixturesover the entire molefraction range of 1,4-BD at four temperaturesT=(303.15,308.15,313.15and 318.15)K*

x_1	U_{Exp}	U_N	U_I	U_V	U_J	U_R	U_C	U_F
1,4-BD + α-picoline								
T=303.15K								
0.0000	1360.2	1360.2	1360.2	1360.2	1360.2	1360.2	1360.2	1360.2
0.1236	1380.9	1384.8	1390.6	1383.9	1379.4	1387.4	1391.8	1382.7
0.2410	1406.0	1409.1	1418.9	1407.6	1399.3	1413.5	1421.0	1405.5
0.3524	1431.8	1433.0	1445.4	1430.9	1419.9	1438.6	1447.9	1428.5
0.4585	1456.3	1456.6	1470.1	1454.2	1441.5	1462.7	1473.0	1451.6
0.5594	1479.6	1479.7	1493.3	1477.2	1463.8	1486.0	1496.3	1474.7
0.6557	1502.1	1502.6	1515.1	1500.1	1487.1	1508.4	1517.9	1497.8
0.7477	1523.8	1525.0	1535.6	1522.9	1511.3	1530.0	1538.0	1520.9
0.8355	1545.3	1547.2	1554.9	1545.5	1536.6	1550.9	1556.7	1544.2
0.9195	1567.0	1568.9	1573.1	1568.0	1562.9	1570.9	1574.2	1567.3
1.0000	1590.4	1590.4	1590.4	1590.4	1590.4	1590.4	1590.4	1590.4
T=308.15K								
0.0000	1340.4	1340.4	1340.4	1340.4	1340.4	1340.4	1340.4	1340.4
0.1236	1367.3	1366.0	1372.2	1364.9	1360.8	1368.7	1373.5	1363.6
0.2410	1394.6	1391.2	1401.8	1389.3	1380.6	1395.8	1403.9	1387.2
0.3524	1422.6	1416.1	1429.4	1413.6	1401.9	1422.0	1432.1	1411.0
0.4585	1448.1	1440.6	1455.2	1437.7	1424.2	1447.2	1458.4	1434.9
0.5594	1472.4	1464.8	1479.4	1461.7	1447.4	1471.5	1482.5	1459.1
0.6557	1495.5	1488.6	1502.1	1485.6	1471.7	1494.9	1504.9	1483.3
0.7477	1517.5	1512.1	1523.4	1509.5	1497.1	1517.4	1525.9	1507.5
0.8355	1539.4	1535.2	1543.5	1533.2	1523.6	1539.2	1545.4	1531.8
0.9195	1561.4	1558.0	1562.5	1556.9	1551.4	1560.2	1563.6	1556.2
1.0000	1580.5	1580.5	1580.5	1580.5	1580.5	1580.5	1580.5	1580.5
T=313.15K								
0.0000	1320.3	1320.3	1320.3	1320.3	1320.3	1320.3	1320.3	1320.3
0.1236	1352.3	1346.7	1353.3	1345.4	1340.4	1349.5	1354.6	1344.1
0.2410	1382.7	1372.8	1384.0	1370.5	1361.4	1377.6	1386.1	1368.4
0.3524	1412.1	1398.5	1412.7	1395.5	1383.3	1404.7	1415.5	1392.9
0.4585	1439.1	1423.9	1439.4	1420.4	1406.2	1430.8	1442.5	1417.8
0.5594	1463.6	1448.9	1464.5	1445.3	1430.2	1456.0	1467.6	1442.7
0.6557	1487.2	1473.6	1488.0	1470.1	1455.4	1480.3	1490.8	1467.9
0.7477	1510.0	1498.0	1510.1	1494.9	1481.8	1503.7	1512.6	1493.1
0.8355	1532.7	1522.1	1530.9	1519.7	1509.5	1526.3	1532.9	1518.4
0.9195	1553.4	1545.8	1550.6	1544.5	1538.6	1548.1	1551.7	1543.7
1.0000	1569.2	1569.2	1569.2	1569.2	1569.2	1569.2	1569.2	1569.2

T=318.15K								
0.0000	1300.4	1300.4	1300.4	1300.4	1300.4	1300.4	1300.4	1300.4
0.1236	1338.2	1327.4	1334.3	1326.0	1320.8	1330.3	1335.6	1324.7
0.2410	1370.3	1354.0	1365.8	1351.5	1342.0	1359.1	1368.2	1349.3
0.3524	1400.9	1380.3	1395.1	1376.9	1364.3	1386.8	1398.0	1374.4
0.4585	1429.0	1406.2	1422.5	1402.4	1387.7	1413.5	1425.8	1399.6
0.5594	1453.7	1431.9	1448.1	1427.8	1412.2	1439.2	1451.4	1425.2
0.6557	1477.5	1457.2	1472.2	1453.3	1437.9	1464.1	1475.2	1451.0
0.7477	1500.6	1482.2	1494.8	1478.7	1464.9	1488.0	1497.6	1476.8
0.8355	1522.8	1506.8	1516.1	1504.2	1493.5	1511.2	1518.2	1502.8
0.9195	1543.0	1531.2	1536.2	1529.7	1523.5	1533.6	1537.3	1528.9
1.0000	1555.2	1555.2	1555.2	1555.2	1555.2	1555.2	1555.2	1555.2
1,4-BD + β-picoline								
T=303.15K								
0.0000	1404.2	1404.2	1404.2	1404.2	1404.2	1404.2	1404.2	1404.2
0.1224	1422.3	1424.4	1428.3	1424.0	1420.6	1426.2	1429.2	1423.1
0.2389	1447.2	1444.2	1450.8	1443.6	1437.5	1447.3	1452.4	1441.9
0.3498	1468.0	1463.6	1472.0	1462.8	1454.9	1467.6	1474.1	1460.8
0.4556	1487.8	1482.7	1491.9	1481.8	1472.7	1487.1	1494.3	1479.6
0.5566	1506.7	1501.5	1510.7	1500.5	1491.0	1505.9	1513.2	1498.3
0.6531	1524.6	1519.9	1528.4	1518.9	1509.8	1524.0	1530.7	1516.9
0.7455	1541.6	1537.9	1545.2	1537.2	1529.1	1541.5	1547.1	1535.5
0.8339	1557.9	1555.7	1561.1	1555.1	1548.9	1558.4	1562.5	1553.9
0.9187	1573.4	1573.2	1576.1	1572.9	1569.4	1574.7	1576.8	1572.2
1.0000	1590.4	1590.4	1590.4	1590.4	1590.4	1590.4	1590.4	1590.4
T=308.15K								
0.0000	1385.0	1385.0	1385.0	1385.0	1385.0	1385.0	1385.0	1385.0
0.1224	1408.8	1406.1	1410.3	1405.6	1402.0	1408.0	1411.3	1404.6
0.2389	1431.9	1426.8	1434.1	1425.9	1419.6	1430.1	1435.7	1424.3
0.3498	1453.7	1447.2	1456.3	1446.1	1437.6	1451.4	1458.5	1444.0
0.4556	1474.3	1467.2	1477.3	1465.9	1456.2	1471.9	1479.8	1463.7
0.5566	1494.1	1486.9	1496.9	1485.6	1475.4	1491.7	1499.6	1483.3
0.6531	1513.0	1506.2	1515.6	1504.9	1495.1	1510.7	1517.9	1502.9
0.7455	1530.9	1525.3	1533.1	1524.2	1515.5	1529.1	1535.1	1522.5
0.8339	1548.2	1544.0	1549.8	1543.1	1536.5	1546.8	1551.2	1541.9
0.9187	1564.5	1562.4	1565.5	1561.9	1558.1	1563.9	1566.3	1561.3
1.0000	1580.5	1580.5	1580.5	1580.5	1580.5	1580.5	1580.5	1580.5
T=313.15K								
0.0000	1365.2	1365.2	1365.2	1365.2	1365.2	1365.2	1365.2	1365.2
0.1224	1391.5	1387.1	1391.6	1386.5	1382.7	1389.1	1392.7	1385.4
0.2389	1415.5	1408.6	1416.4	1407.6	1400.8	1412.2	1418.2	1405.8
0.3498	1438.4	1429.8	1439.7	1428.4	1419.5	1434.4	1442.0	1426.3
0.4556	1460.1	1450.7	1461.5	1449.1	1438.8	1455.7	1464.2	1446.8
0.5566	1480.7	1471.3	1482.1	1469.6	1458.7	1476.4	1484.8	1467.3
0.6531	1500.4	1491.5	1501.5	1489.9	1479.3	1496.3	1504.1	1487.8
0.7455	1519.0	1511.4	1519.8	1509.9	1500.6	1515.5	1522.0	1508.2
0.8339	1536.8	1530.9	1537.2	1529.9	1522.7	1533.9	1538.7	1528.7
0.9187	1553.7	1550.2	1553.6	1549.6	1545.5	1551.9	1554.4	1548.9
1.0000	1569.2	1569.2	1569.2	1569.2	1569.2	1569.2	1569.2	1569.2
T=318.15K								
0.0000	1345.3	1345.3	1345.3	1345.3	1345.3	1345.3	1345.3	1345.3
0.1224	1373.6	1367.8	1372.6	1367.1	1363.2	1369.9	1373.6	1366.0
0.2389	1398.6	1389.9	1398.1	1388.6	1381.7	1393.6	1399.9	1386.9
0.3498	1422.2	1411.7	1422.0	1410.0	1400.8	1416.4	1424.4	1407.9
0.4556	1444.6	1433.2	1444.5	1431.2	1420.6	1438.4	1447.2	1428.9
0.5566	1466.1	1454.3	1465.6	1452.3	1441.1	1459.6	1468.4	1450.0
0.6531	1486.4	1475.1	1485.6	1473.2	1462.3	1480.1	1488.2	1471.1
0.7455	1505.5	1495.6	1504.4	1493.9	1484.3	1499.8	1506.6	1492.2
0.8339	1523.7	1515.8	1522.3	1514.5	1507.0	1518.9	1523.8	1513.3
0.9187	1540.8	1535.6	1539.2	1534.9	1530.7	1537.4	1539.9	1534.3
1.0000	1555.2	1555.2	1555.2	1555.2	1555.2	1555.2	1555.2	1555.2

Table3. *Average percentage deviations for various speeds of sound relationsat fourtemperatures T=(303.15, 308.15, 313.15 and 318.15) K*

T/K	$\%U_N$	$\%U_I$	$\%U_V$	$\%U_J$	$\%U_R$	$\%U_C$	$\%U_F$
1,4-BD + α-picoline							
303.15	-0.1099	-0.7884	0.0156	0.6817	-0.4223	-0.9388	0.1463
308.15	0.3482	-0.3874	0.5011	1.2160	0.0128	-0.5458	0.6352
313.15	0.7820	-0.0068	0.9636	1.7226	0.4255	-0.1661	1.0962
318.15	1.2200	0.3883	1.4242	2.2190	0.8465	0.2180	1.5610
1,4-BD + β-picoline							
303.15	0.1947	-0.2609	0.2416	0.7046	-0.0237	-0.3780	0.3477
308.15	0.3539	-0.1459	0.4183	0.9209	0.1170	-0.2704	0.5290
313.15	0.4861	-0.0567	0.5699	1.1099	0.2314	-0.1892	0.6845
318.15	0.6264	0.0550	0.7294	1.2921	0.3606	-0.0806	0.8430

Table4. *The average values of Chi-square for seven theories at 303.15 K*

System	U_N	U_I	U_V	U_J	U_R	U_C	U_F
1,4-BD+α-picoline	0.0028	0.0948	0.0022	0.0853	0.0267	0.1349	0.0067
1,4-BD+β-picoline	0.0095	0.0107	0.0133	0.0906	0.0015	0.0220	0.0247

Table5. *Molecular association, α, for the two mixtures at four temperatures T = (303.15, 308.15, 313.15 and 318.15) K*

x_1	303.15 K	308.15K	313.15K	318.15K
1,4-BD + α-picoline				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1236	-0.0044	0.0035	0.0102	0.0185
0.2410	-0.0022	0.0076	0.0179	0.0280
0.3524	0.0012	0.0128	0.0239	0.0351
0.4585	0.0029	0.0145	0.0264	0.0383
0.5594	0.0032	0.0147	0.0254	0.0365
0.6557	0.0026	0.0133	0.0233	0.0336
0.7477	0.0012	0.0107	0.0202	0.0298
0.8355	-0.0003	0.0081	0.0172	0.0249
0.9195	-0.0013	0.0058	0.0116	0.0175
1.0000	0.0000	0.0000	0.0000	0.0000
1,4-BD + β-picoline				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1224	-0.0025	0.0045	0.0072	0.0096
0.2389	0.0050	0.0083	0.0113	0.0144
0.3498	0.0072	0.0106	0.0139	0.0173
0.4556	0.0082	0.0114	0.0152	0.0188
0.5566	0.0083	0.0115	0.0152	0.0191
0.6531	0.0075	0.0107	0.0142	0.0181
0.7455	0.0058	0.0089	0.0121	0.0156
0.8339	0.0035	0.0066	0.0091	0.0122
0.9187	0.0006	0.0033	0.0053	0.0078
1.0000	0.0000	0.0000	0.0000	0.0000

The experimental values of speeds of sound are found to follow an increasing trend with the increase in mole fraction of 1,4-BD (x_1). A look at Table 2 clearly indicates that the Rao's approach gives the best results amongst all the other approaches except at 303.15 K. The second best results are found to be given by the Van Dael ideal mixing relation. The highest deviation is obtained by the Junjie relation followed by CFT. However, we find that the computed values of speeds of sound exhibit similar trend as that of the experimental. The APD values (Table 3) clearly indicate that the lowest values are from the Nomoto's approach and the highest ones are through the Jungie. The same results are observed for both the mixtures under study.

Both positive and negative deviations are observed for the systems under study. The positive deviations in speeds of sound are attributed to two factors, (i) molecular association and (ii) complex formation whereas negative deviations are due to molecular dissociation of an unassociated species caused by addition of an inert solvent or an active solvent. The actual sign and magnitude of the deviations observed experimentally would depend on the relative strength of the two opposing effects, molecular association and dissociation.

The study of Table 3 reveals that the values of APD for the U_N, U_I,U_V, U_J, U_R, U_C and U_F are in the range from -0.1099 to 1.22, -0.7884 to 0.388, 0.0156 to 1.4242, 0.6817 to 2.2190, -0.4223 to 0.8465, -0.0806 to -0.9388 and 0.1463 to 1.5610respectively for the two binary mixtures at four temperatures investigated. The average APD for the Impedance relation and Rao's Specific velocity are comparatively less than those found for other estimations.

Thus, the estimation ability of speed of sound in the present investigated mixtures follows the sequence U_R> U_V> U_I> U_N> U_F > U_C> U_J. The ratio U_{exp}^2/U_{imx}^2 is used as an important tool to measure the nonideality in the mixtures, especially in those cases where the properties other than speeds of sound are not known.

Fig. 1(a, b) represent the variation of U_{exp}^2/U_{imx}^2 with mole fraction of 1,4-BD for the two binary mixtures at different temperatures. Both the graphs show similar trends at all temperatures studied. A perusal of the figures 1(a) and 1(b) shows that the values are on the higher side for the α-picoline system as compared to the β-counterpart. A slight lower trend is observed at x_1=0.12 in the two mixtures at T=303.15 K. same can be observed in Table 5 (negative values of α).The interaction parameter characterizing a system varies with the composition, molar mass and temperature. It is employed to account for the contribution of non-combinational entropy of mixing and the enthalpy of mixing to the Gibbs energy of mixing. When the values of interaction parameter, α, show positive sign, it represents strong interaction between the mixing molecules. On increasing the temperature the speeds of sound values decrease in the two binary mixtures. This is probably due to the fact that thermal energy activates the molecules, which would increase the rate of association of unlike molecules [20,21].

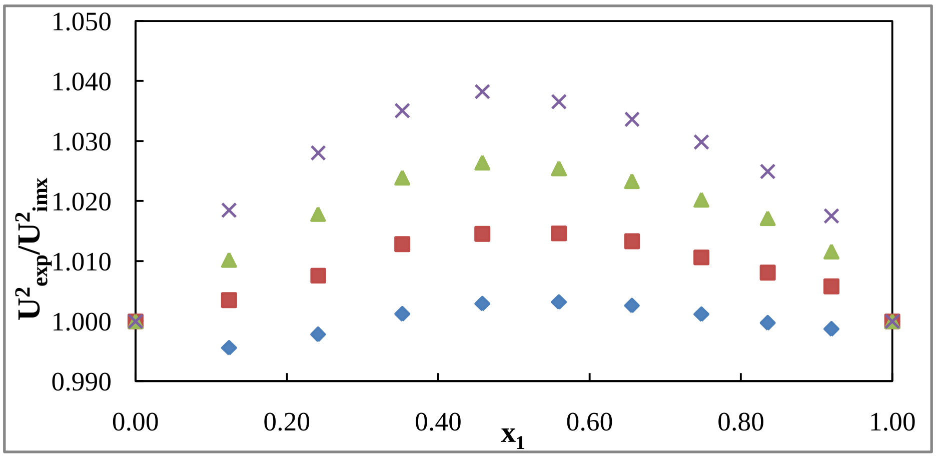

Fig1(a). *The variations of U_{exp}^2/U_{imx}^2 in the binary liquid mixture1,4-BD + α-picolineover the entire mole fraction range of 1,4-BD at temperatures T = (303.15 (♦), 308.15 (■), 313.15 (▲) and 318.15 (×)) K*

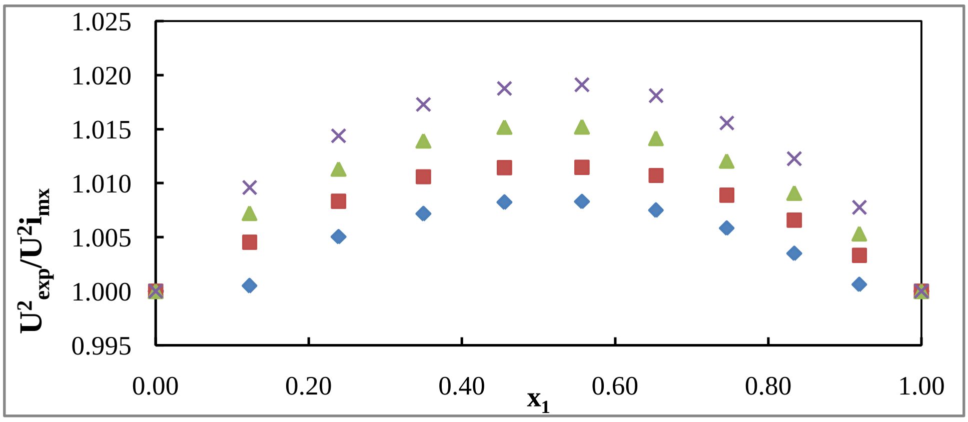

Fig1(b). *The variations of U_{exp}^2/U_{imx}^2 in the binary liquid mixture1,4-BD + β-picoline over the entire mole fraction range of 1,4-BD at temperatures T = (303.15 (♦), 308.15 (■), 313.15 (▲) and 318.15 (×)) K*

5. CONCLUSIONS

Speeds of sound evaluated using Nomoto (N), impedance (I), Van-Dael and Vangeel (V), Junjie (J), Rao's specific velocity (R), Collision factor theory (C) and Free length theory (F) have been compared with the experimentally measuredspeeds of sound values at temperatures T=(303.15,308.15,313.15 and 318.15)K.It may be concluded that Nomoto's relation, Van-Dael ideal mixing relation have provided good results.The observed deviation of theoretical values of speeds of sound from the experimental values is attributed for the presence of molecular interactions in the system studied.Further the magnitude of the ratio of U^2_{exp}/U^2_{imx} in the present system at all the temperatures clearly indicate the existence of strong tendency for theformation of associationbetween the component molecules of the liquid mixtures.

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