



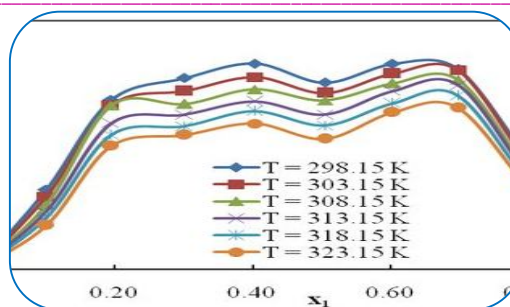
ESTIMATION OF THEORETICAL ULTRASONIC VELOCITIES OF BINARY LIQUID MIXTURE OF ANILINE WITH O-XYLENE AT TEMPERATURES $T = (303.15, 308.15, 313.15 \text{ AND } 318.15) \text{ K}$

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ABSTRACT :

At temperatures $T = (303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}$, Ultrasonic velocities, viscosities and densities in a binary liquid mixture containing Aniline with o-Xylene are measured over the entire mole fraction range of aniline. Ultrasonic velocities have been evaluated theoretically 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 deviations from experimental values are analyzed in terms of molecular interaction parameter. U^2_{EXP}/U^2_{IMX} is also estimated for non-ideality in the liquid mixtures. The results arrived at in the comparison are discussed and represented graphically.

KEYWORDS : Ultrasonic velocity; Nomoto's Relation; Junjie's relation; aniline; temperature.

INTRODUCTION

Ultrasonic velocity measurement data proves to be a very easy and suitable tool to find out various thermodynamic properties of liquids and liquid mixtures. Several researchers carried out ultrasonic analysis on liquid mixtures and draw a parallel to the experimental results. In the present paper we discuss the theoretical values of ultrasonic velocity in binary liquid mixture containing Aniline with o-Xylene at temperatures $T = (303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}$ over the entire mole fraction range of Aniline. The results are evaluated by using Nomoto, impedance relation, Van Dael and Vangeel ideal mix relations, Junjie and Rao's Specific velocity relations and have been compared with the experimental values. The results are inferred in terms of molecular interaction parameter to explain molecular association between the component molecules of the binary liquid mixture and also the typical nature of the molecular association in the liquid mixture is examined by the variation of U^2_{EXP}/U^2_{IMX} .

EXPERIMENTAL SECTION

Ultrasonic pulse echo interferometer (Mittal enterprises, India) is used for ultrasonic velocities measurements and all these observations 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. Specific gravity bottle is utilized 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. Ostwald's viscometer is employed for the

measurement of viscosity of pure liquids or liquid mixtures. The time of flow of liquid in the viscometer is estimated with an electronic stopwatch with a precision of 0.01s.

THEORY

The following equations are used to estimate ultrasonic velocities theoretically in binary liquid mixture are as follows,

(1). Nomoto's Relation:

$$U_{\text{NOM}} = [(X_1 R_1 + X_2 R_2) / (X_1 V_1 + X_2 V_2)]^3 \quad \text{-----(1)}$$

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 Relation:

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

Where X_i is the mole fraction, ρ_i the density of the mixture and Z_i is the acoustic impedance.

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

$$U_{\text{VDV}} = [(X_1/M_1 U_1^2 + X_2/M_2 U_2^2) (X_1 M_1 + X_2 M_2)]^{-1/2} \quad \text{-----(3)}$$

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

(4). Jungie's Equation:

$$U_{\text{JUN}} = (X_1 M_1 / \rho_1 + X_2 M_2 / \rho_2) / \{ [X_1 M_1 + X_2 M_2]^{1/2} [X_1 M_1 / \rho_1 U_1^2 + X_2 M_2 / \rho_2 U_2^2] \}^{1/2} \quad \text{-----(4)}$$

Where ρ_1 and ρ_2 are the densities of constituent components.

(5). Rao's specific velocity Equation:

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

Where X_i is the mole fraction and ρ_i is the density of the mixture.

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

$$(\Delta U/U) \% = ((U_{\text{EXP}} - U_{\text{THEORY}}) / (U_{\text{EXP}})) \times 100 \quad \text{-----(6)}$$

The inter molecular interaction parameter (α) is given by

$$\alpha = U_{\text{EXP}}^2 / U_{\text{IMX}}^2 - 1 \quad \text{-----(7)}$$

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocities along with the theoretically evaluated values by using various theories in the binary liquid mixture containing Aniline with o-Xylene at temperatures T = (303.15, 308.15, 313.15 and 318.15) K are given in **TABLE-1**. The percentage deviations in experimental and theoretical ultrasonic velocity values in the binary liquid mixture containing Aniline with o-Xylene at temperatures T = (303.15, 308.15, 313.15 and 318.15) K are presented in **TABLE-2**.

The values of $U_{\text{EXP}}^2/U_{\text{IMX}}^2$ and molecular interaction parameter (α) in the binary liquid mixture containing Aniline with o-Xylene at temperatures T= (303.15, 308.15, 313.15 and 318.15) K are quoted in TABLE-3.

TABLE-1: Experimental and theoretical values of ultrasonic velocities in the binary liquid mixture containing (Aniline + o-Xylene) over entire mole fraction range of Aniline at four temperatures T = (303.15, 308.15, 313.15 and 318.15) K.

Mole fraction of Aniline (X)	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	1339.93	1339.93	1339.93	1339.93	1314.1500	1339.93
0.0146	1370.23	1365.83	1344.61	1363.25	1377.5612	1343.69
0.0323	1398.86	1392.06	1350.24	1389.88	1403.7947	1348.25
0.0541	1428.17	1418.63	1357.14	1418.19	1430.3626	1353.89
0.0816	1458.64	1445.54	1365.79	1446.66	1457.2671	1361.05
0.1176	1489.77	1472.78	1376.98	1476.79	1484.5101	1370.44
0.1667	1519.88	1500.36	1391.99	1505.9	1512.0940	1383.29
0.2373	1544.51	1528.29	1413.18	1530.53	1540.0208	1401.94
0.3478	1574.14	1556.56	1445.39	1562.16	1568.2926	1431.47
0.5455	1600.77	1585.18	1500.17	1591.79	1596.9116	1485.29
1.0000	1614.15	1614.15	1614.15	1614.15	1614.1500	1614.15
T=308.15K						
0.0000	1314.52	1314.52	1314.52	1314.52	1314.52	1314.52
0.0146	1346.48	1340.88	1319.20	1339.5	1359.31	1318.31
0.0323	1376.09	1367.54	1324.83	1367.11	1388.92	1322.91
0.0541	1405.70	1394.49	1331.73	1395.72	1418.53	1328.60
0.0816	1435.61	1421.74	1340.40	1423.63	1448.44	1335.82
0.1176	1466.82	1449.28	1351.60	1453.84	1479.65	1345.28
0.1667	1498.47	1477.12	1366.65	1484.49	1511.30	1358.24
0.2373	1522.90	1505.26	1387.94	1508.92	1535.73	1377.06
0.3478	1551.01	1533.69	1420.34	1539.03	1563.84	1406.86
0.5455	1577.97	1562.42	1475.65	1568.99	1582.62	1461.20
1.0000	1591.45	1591.45	1591.45	1591.45	1591.45	1591.45
T=313.15K						
0.0000	1298.45	1298.45	1298.45	1298.45	1298.45	1298.45
0.0146	1332.17	1324.51	1302.99	1325.19	1341.69	1302.17
0.0323	1361.78	1350.81	1308.45	1352.8	1371.30	1306.67
0.0541	1391.39	1377.35	1315.15	1381.41	1400.91	1312.24
0.0816	1421.30	1404.12	1323.57	1409.32	1430.82	1319.32
0.1176	1452.51	1431.13	1334.46	1439.53	1462.03	1328.59
0.1667	1484.16	1458.37	1349.10	1470.18	1493.68	1341.29
0.2373	1508.59	1485.85	1369.83	1494.61	1518.11	1359.72
0.3478	1536.70	1513.55	1401.45	1524.72	1546.22	1388.91
0.5455	1563.66	1541.49	1455.60	1554.68	1573.18	1442.13
1.0000	1569.65	1569.65	1569.65	1569.65	1569.65	1569.65
T=318.15K						
0.0000	1278.98	1278.98	1278.98	1278.98	1278.98	1278.98
0.0146	1317.86	1305.40	1283.48	1310.88	1329.57	1282.71

0.0323	1347.47	1332.01	1288.90	1338.49	1359.18	1287.22
0.0541	1377.08	1358.80	1295.55	1367.1	1388.79	1292.81
0.0816	1406.99	1385.77	1303.92	1395.01	1418.70	1299.90
0.1176	1438.20	1412.92	1314.75	1425.22	1449.91	1309.21
0.1667	1469.85	1440.25	1329.32	1455.87	1481.56	1321.94
0.2373	1494.28	1467.74	1350.00	1480.3	1505.99	1340.43
0.3478	1522.39	1495.41	1381.60	1510.41	1534.10	1369.72
0.5455	1549.35	1523.24	1435.93	1540.37	1561.06	1423.14
1.0000	1551.23	1551.23	1551.23	1551.23	1551.23	1551.23

TABLE 2: Percentage deviations between experimental and theoretical values of ultrasonic velocities in the binary liquid mixture containing (Aniline + o-Xylene) over entire mole fraction range of Aniline at four temperatures T = (303.15, 308.15, 313.15 and 318.15) K.

Mole fraction of Aniline (X)	%U _{NOM}	%U _{IMP}	%U _{VDV}	%U _{JUN}	%U _{RAO}
T=303.15K					
0.0000	0.0000	0.0000	0.0000	-1.9240	0.0000
0.0146	-0.3210	-1.8699	0.5094	0.5350	-1.9368
0.0323	-0.4858	-3.4759	0.6420	0.3528	-3.6179
0.0541	-0.6678	-4.9737	0.6988	0.1535	-5.2010
0.0816	-0.8983	-6.3652	0.8213	-0.0941	-6.6904
0.1176	-1.1404	-7.5710	0.8713	-0.3531	-8.0100
0.1667	-1.2841	-8.4146	0.9198	-0.5123	-8.9870
0.2373	-1.0501	-8.5028	0.9051	-0.2907	-9.2308
0.3478	-1.1166	-8.1793	0.7611	-0.3715	-9.0636
0.5455	-0.9738	-6.2842	0.5610	-0.2410	-7.2143
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
0.0146	-0.4158	-2.0262	0.5184	0.9529	-2.0920
0.0323	-0.6214	-3.7253	0.6526	0.9324	-3.8647
0.0541	-0.7974	-5.2622	0.7100	0.9127	-5.4851
0.0816	-0.9662	-6.6322	0.8345	0.8937	-6.9513
0.1176	-1.1956	-7.8548	0.8849	0.8747	-8.2856
0.1667	-1.4246	-8.7967	0.9330	0.8562	-9.3580
0.2373	-1.1584	-8.8621	0.9180	0.8425	-9.5765
0.3478	-1.1165	-8.4247	0.7724	0.8272	-9.2941
0.5455	-0.9853	-6.4840	0.5691	0.2947	-7.4002
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
0.0146	-0.5750	-2.1907	0.5240	0.7146	-2.2523
0.0323	-0.8056	-3.9164	0.6594	0.6991	-4.0470
0.0541	-1.0093	-5.4796	0.7173	0.6842	-5.6884
0.0816	-1.2087	-6.8764	0.8429	0.6698	-7.1754
0.1176	-1.4720	-8.1276	0.8936	0.6554	-8.5313
0.1667	-1.7376	-9.1003	0.9419	0.6414	-9.6265
0.2373	-1.5077	-9.1981	0.9267	0.6311	-9.8682
0.3478	-1.5064	-8.8013	0.7796	0.6195	-9.6176

0.5455	-1.4181	-6.9110	0.5743	0.6088	-7.7724
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
0.0146	-0.9453	-2.6088	0.5296	0.8886	-2.6676
0.0323	-1.1473	-4.3467	0.6664	0.8690	-4.4712
0.0541	-1.3274	-5.9203	0.7247	0.8504	-6.1195
0.0816	-1.5080	-7.3258	0.8515	0.8323	-7.6110
0.1176	-1.7576	-8.5838	0.9025	0.8142	-8.9690
0.1667	-2.0141	-9.5605	0.9511	0.7967	-10.0628
0.2373	-1.7761	-9.6556	0.9356	0.7837	-10.2957
0.3478	-1.7725	-9.2477	0.7869	0.7692	-10.0283
0.5455	-1.6855	-7.3205	0.5796	0.7558	-8.1461
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE-3: Values of U^2_{EXP}/U^2_{IMX} and molecular interaction parameter (α) in the binary liquid mixture containing (Aniline + o-Xylene) over entire mole fraction range of Aniline at four temperatures T = (303.15, 308.15, 313.15 and 318.15) K.

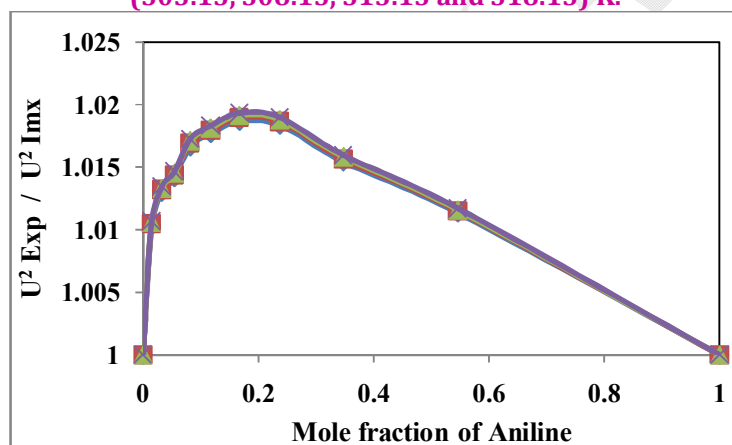
Mole fraction (X)	At T=303.15K	At T=308.15K	At T=313.15K	At T=318.15K
U^2_{EXP}/U^2_{IMX}				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0146	0.0103	0.0104	0.0106	0.0107
0.0323	0.0130	0.0132	0.0133	0.0135
0.0541	0.0141	0.0144	0.0145	0.0147
0.0816	0.0166	0.0169	0.0171	0.0172
0.1176	0.0177	0.0179	0.0181	0.0183
0.1667	0.0187	0.0189	0.0191	0.0193
0.2373	0.0184	0.0186	0.0188	0.0190
0.3478	0.0154	0.0156	0.0158	0.0159
0.5455	0.0113	0.0115	0.0116	0.0117
1.0000	0.0000	0.0000	0.0000	0.0000
Molecular interaction parameter (α)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0146	0.0103	0.0104	0.0106	0.0107
0.0323	0.0130	0.0132	0.0133	0.0135
0.0541	0.0141	0.0144	0.0145	0.0147
0.0816	0.0166	0.0169	0.0171	0.0172
0.1176	0.0177	0.0179	0.0181	0.0183
0.1667	0.0187	0.0189	0.0191	0.0193
0.2373	0.0184	0.0186	0.0188	0.0190
0.3478	0.0154	0.0156	0.0158	0.0159
0.5455	0.0113	0.0115	0.0116	0.0117
1.0000	0.0000	0.0000	0.0000	0.0000

TABLE-1 illustrates the deviations of theoretical values obtained by various theories with experimental values. The limitations and approximations included in these theories are because of

various types of forces such as dispersion forces, charge transfer, hydrogen bonding and dipole-induced dipole interactions between molecules take place on mixing with each other. These monitored differences of ultrasonic velocity values from the experimental values point out the existence of molecular interactions between the unlike molecules in the liquid mixture. From **TABLE-2**, it demonstrates the negative and positive percentage deviations of the ultrasonic velocity in the binary liquid mixture. These types of negative and positive percentage deviations specify the non-ideal behavior of liquid mixture. In such cases the ratio of U^2_{EXP}/U^2_{IMX} is an important tool to measure the non-ideality in liquid mixture.

FIGURE-1 clearly designates that ratio of U^2_{EXP}/U^2_{IMX} increases from unity with the increase of mole fraction from 0 to 0.5, above the 0.5 mole fraction range the ratio of U^2_{EXP}/U^2_{IMX} decreases and tends to unity at all the observed temperatures in (Aniline + o-Xylene) liquid mixture. Also the deviations of the ratio U^2_{EXP}/U^2_{IMX} from unity are a direct measure of non-ideality of the system as a consequence of association or other type of dipole-induced dipole interactions. These types of specific interactions are explained by using molecular interaction parameter (α). The positive values of α clearly indicate the existence of strong interactions in the liquid mixture studied. **TABLE-3** also specifies that, α decreases with the increase of temperature which clearly suggests that interaction becomes weak with the rise of temperature.

FIGURE-1: The variations of U^2_{EXP}/U^2_{IMX} in (Aniline + o-Xylene) liquid mixture at temperatures T = (303.15, 308.15, 313.15 and 318.15) K.



CONCLUSIONS

Experimentally measured values of ultrasonic velocities for the binary liquid mixture of Aniline + o-Xylene at temperatures T = (303.15, 308.15, 313.15 and 318.15)K are compared with the values estimated theoretically by Nomoto (U_{NOM}), impedance (U_{IMP}), Van-Dael and Vangeel (U_{VDV}), Junjie (U_{JUN}) and Rao's specific velocity (U_{RAO}) models. Comparison of these values concludes that Nomoto's and Junjie's relations give less deviation from the experimental values whereas; the remaining theories show large deviations. The observed deviation of theoretical values of velocity from the experimental values feature the presence of molecular interactions in the system studied. Also the positive values of α clearly point towards the existence of strong tendency for the formation of association between the component molecules of the liquid mixture.

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