RESEARCH ARTICLE

Theories of Ultrasonic Velocities and their Application in Binary Liquid Mixtures of *N*-Ethylaniline with Some Toluenes (Toluene, *o*-Nitrotoluene and *m*-Nitrotoluene)

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Abstract: Ultrasonic velocities and densities of the binary liquid mixtures of *N*-ethyl aniline with different toluenes like toluene, *o*-nitrotoluene and *m*-nitrotoluene have been measured at temperatures 303.15 and 308.15 K over the entire composition range. Various theories of ultrasonic velocity were applied to experimental values in evaluating the velocities using Nomoto's relation (U_{NR}), Impedence relation (U_{IR}), Ideal mixing relation (U_{IMR}), Jungie's relation (U_{IR}) and Rao's specific velocity relation (U_R). The molecular interaction parameter (χ) has been evaluated from the values of experimental and theoretical velocities. The variation of this interaction parameter with the composition mixture has been discussed in terms of molecular interactions.

Keywords: Ethyl aniline, Theoretical velocities, Ultrasonics, Hydrogen bonding, Interaction parameter

Introduction

In recent years measurement of ultrasonic investigations find extensive applications in determining the physicochemical behavior of liquid mixtures¹⁻⁵. Several researchers⁶⁻⁹ carried out ultrasonic investigations and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto¹⁰, Van Deal and Vangeel ideal mix relations¹¹ impedance relation¹² Rao's Specific velocity¹³ and Junjie¹⁴ and interpreted the results in terms of molecular interactions. Ultrasonic study of liquid mixtures, due to its non destructive nature, has been extensively carried out in different branches of science to measure the thermodynamic properties and to predict the nature of molecular interaction between the molecules in a medium. The ultrasonic sound velocity and the thermodynamic parameters derived from it have been widely used to interpret the interactions between unlike molecules in the binary liquid mixtures.Longeman and Correy¹⁵ discussed sound velocity in a liquid as the sum of bond velocities. Randall¹⁶ has shown a close agreement between the experimental and theoretical values calculated from the adiabatic compressibility measurements. Auslander *et al.*,¹⁷, Samal *et al.*,¹⁸, Aziz *et al.*,^{19,20} and Younglove²¹ showed

that there is close relation between sound velocity and thermodynamic properties. This investigation presents the application and evaluation of ultrasonic velocity theories like Nomoto's relation, ideal mixing relation, impedance relation, Rao's specific velocity relation and Junjie's relations for the binary mixtures of Ethyl aniline and toluene, *o*-nitrotoluene and *m*-nitro toluene at temperatures 303.15 and 308.15 K ,over the entire composition range. An attempt has been made to study the molecular interactions from the deviation values in U^2/U^2_{imix} from unity based on earlier studies^{22,23}.

Experimental

Ethlyaniline (Merck India >0.995 purity) was distilled at low pressure and over freshly activated 0.3 nm molecular sieves²⁴. Other compounds under study as mentioned above (SD Fine Chemicals, India, with purity >0.995) were purified by methods described in the literature²⁵. The purity of the chemicals was verified further by measuring the densities and ultrasonic velocities which are in good agreement with the literature values.

Apparatus and procedure

The ultrasonic velocity of sound (U) was measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi model -F05) operating at 2 MHz. with a precision of 0.8 m.s⁻¹ and an uncertainty less than ± 0.1 m.s⁻¹. The temperature stability was maintained within ± 0.01 K by circulating water bath around the measuring cell through a pump.

The densities, ρ , of pure liquids and their mixtures are determined using a 10^{-5} m³ double-arm pycnometer, and the values from triplicate replication at each temperature are reproducible within $2x10^{-1}$ kg m³ and the uncertainty in the measurement of density is found to be 2 parts in 10^4 parts. The reproducibility in mole fractions was within ±0.0002.

Theory

Comparison of theoretical values of ultrasonic velocities with those obtained experimentally in binary liquid mixtures is expected to reveal the nature of interaction between component molecules. The measured values of ultrasonic velocity in the binary liquid mixtures were subjected to theoretical prediction and comprehensive theoretical model of prediction has been evaluated. Following are various theories adopted.

Nomotos relation (U_{NR})

On assuming the additivity of molar sound velocity(R) and no volume change on mixing, Nomoto established the following relation for the ultrasonic velocity of binary liquid mixtures

$$R = M/\rho U^{1/3}$$
(1)

Where U and ρ are determined experimentally and M is the mean molecular weight in a binary liquid mixture

$$\mathbf{M} = (\mathbf{X}_1 \mathbf{M}_1 + \mathbf{X}_2 \mathbf{M}_2) \tag{2}$$

Where M_1 and M_2 are molecular weights of constituent components. Simple manipulation yields the following relation

$$U_{NR} = \left[\left(X_1 R_1 + X_2 R_2 \right) / \left(X_1 V_1 + X_2 V_2 \right) \right]^3$$
(3)

Impedance relation (U_{IR})

Impedance is the product of ultrasonic velocity (U) and the density (ρ) of a liquid mixture. Hence the impedance relation predicts the ultrasonic velocity of the given mixture by simply using the values of impedance (Z_i) and the density (ρ) values. Impedance relationis given as

$$U_{\rm IR} = \Sigma X_i Z_i \Sigma X_i \rho_i \tag{4}$$

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

Jungie equation (U_J)

The Junjie equation is given as

$$U_{J} = (X_{1}M_{1}/\rho_{1} + X_{2}M_{2}/\rho_{2}) / [\{X_{1}M_{1} + X_{2}M_{2}\}^{1/2} \{X_{1}M_{1}/\rho_{1}U_{1}^{2} + X_{2}M_{2}/\rho_{2}U_{2}^{2})\}^{1/2}]$$
(5)

Where M_1 , M_2 are molecular weights of constituent components. ρ_1 and ρ_2 are the densities of constituent components.

Rao's specific velocity method relation (U_R)

Rao's specific velocity method¹¹ U_R = $(\Sigma X_i r_i d)^3$ (6)

Where Xi is the mole fraction, U_i the ultrasonic velocity and ρ_{1} the density of the mixture. r_i is the Rao's specific sound velocity, which is given by $r_i = Ui^{1/3}/\rho_i$ and Z_i is the acoustic impedance.

Ideal mixing relation (U_{imix})

Van Deal and Vangeel (1969) suggested the following relation for the velocity of sound

$$1/(X_1M_1 + X_2M_2) * 1/U_{\text{imix}}^2 = X_1/M_1U_1^2 + X_2/M_2U_2^2$$
(7)

Where U_{imix} is the ideal mixing ultrasonic velocity in liquid mixture and U_1 and U_2 are the velocities of the individual components. The degree of molecular interaction given as interaction parameter (χ)

$$= (U^{2} exp/U^{2}_{imix})^{-1}$$
(8)

Percentage deviation = $(\Delta U/U) \% = [(U_{exp}-U_{theoritical}/U_{exp}]*100$ (9)

Results and Discussion

Amines are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group. The aromatic ring decreases the alkalinity of the amine, depending on its substituents, while the presence of an amine group strongly increases the reactivity of the aromatic ring, due to an electron-donating effect.

When a methyl group is introduced into the aromatic ring, it causes to change in the π - electron density around the aromatic ring²⁶ because of positive mesomeric and positive electromeric effects. (+T effect > -I effect). Further, substitution of $-NO_2$ group at ortho and meta positions of benzene molecule increase the distance of closest approach of the *N*-ethyl aniline molecule resulting decrease in interaction between component molecules. Toluene is more reactive or activated with respect to benzene. It is a fact that the effect of substituents on a benzene ring have on both the rate and orientation of electrophilic aromatic substitution reactions. These effects are a combination of resonance and inductive effects. The substituent -NO₂ is an electron withdrawing group that removes electron density from the π -system making it less nucleophilic. Besides the electronic effects, influences from steric effects are also to be considered. The effect on the π -electron density due to methyl group is relatively small, which tends to decrease the magnitude of V^E. The difference in shapes of molecules with the addition of methyl and - NO₂ groups also leads to different alignments in the liquid mixtures. Further, the electron donor-acceptor interactions tend to decrease with additional functional groups.



With this above explanation in understanding the molecular interactions, we further extended our study in testing the validity of various theoretical approaches of ultrasonic velocity for liquids in the aforementioned binary systems by comparing theoretical sound speeds with those experimentally determined in the temperature range 303.15-318.15 K. The experimental values of sound speed for the systems along with theoretical values and percentage deviations for Nomoto's Relation (U_{NR}), Vandeal Vangael Ideal Mixing Relation (U_{IMR}), Impedance Relation (U_{IR}) , Rao's specific velocity method (U_{R}) and Junjie's relation (U_{J}) are compared for all the five binaries. 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. Again, no molecular interaction is taken into account. Similarly, as per the assumption for the Collision Factor theory, the molecules are treated as real non- elastic substances, which is not really the case. But on mixing two liquids, the interaction between the molecules of the two liquids takes place because of presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole dipole and dipole – induced dipole interactions. Thus, the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture. It can be seen from Tables 1-3 that the theoretical values of ultrasonic velocity computed by various theories show deviations from experimental values. In general the predictive ability of various ultrasonic theories depends upon the strength of interactions that exist in a binary system. In case of strong interactions existing between the molecules of the mixtures there is much deviation in theoretical prediction of velocity than the molecules of the mixture where less interaction is observed.

Data reveal that the sound speed computed from impedance relation, U_{imr} exhibit more satisfactory agreement with the experimental values in the temperature range 303.15 K-318.15 K than other approaches in the binary systems *N*-ethyl aniline + toluene.

Table 1 show that in the system of *N*-ethylaniline + toluenethere is good agreement between experimental and theoretical values calculated by impedance and Nomoto relations. Here Nomoto relation provides the best result than theImpedance relation at all the temperatures. However, higher deviations are observed in Rao's specific and slight variations in Junjie's theories. Ethyl aniline+ *o*-nitro toluene system, as described in Table 2, there is good agreement between experimental and theoretical values in Nomoto relation followed by impedance relations where as higher deviations are observed in VanDael ideal mixing relation, Rao's specific velocity method and Junjie's relation. Ethyl aniline and mnitro toluene, Ethyl aniline+ *o*-nitro toluene system, as described in Table 3 showed good agreement between experimental and theoretical values calculated by Rao's specific velocity method and impedance relation. Here Rao's specific velocity method provides the best result than the result of impedance relation at all temperatures. However, higher deviations are observed in Nomoto's relation, Van Dael ideal mixing relation and Junjie's theory. Table 4 shows the U^2_{exp}/U^2_{imx} values from the the derived velocity values for these systems. The percentage deviations of the ultrasonic velocity are both negative and positive. Such deviations indicate the non-ideal behavior of liquid mixtures. The ratio U_{exp}^2/U_{imx}^2 is used as an important tool to measure the non-ideality in the mixtures, especially in these cases where the properties other than sound velocity are not known .A perusal of values indicate small deviations from ideality, which may be due to the existence of weak tendency for the formation of association in liquid mixtures.

Looking into the behavior of all three binary mixtures, it can be understood that, positive deviation in velocity are attributed to the molecular associations, complex formations, whereas negative deviations indicate molecular dissociations of an associated species by the addition of solvent. In our investigation, all systems showed positive deviations with lower magnitude, indicating weak interactions. Maximum positive values for U_{exp}^2/U_{imix}^2 are observed in case of Ethyl aniline+ *m*-nitro toluene(1.164 at 308.15 K), than Ethyl aniline+ *o*-nitro toluene (1.133 at 303.15 K) at nearly equimolar composition at all measured temperatures due to specific interactions/complex formations between unlike molecules through hydrogen bonding. Ethyl aniline+toluene systems also showed decreasing values for U_{exp}^2/U_{imix}^2 , as revealed from Table 4. The U_{exp}^2/U_{imix}^2 values of all five binaries have been shown in table 4.

Table 1-3. Values of experimental ultrasonic velocities and evaluated theoretical velocities along with percentage deviations and interaction parameters for the studied systems at temperatures 303.15K-308.15K

x1	Uexp	Unomoto	Uimx	Uir	Urao	Uj	%Unom	ı%Uimx	%Uir	%Ur	%Uj	α
0	1278	1278	1278	1278	1278	1278	0	0	0	0	0	0
0.0612	1298.3	1292.5	1295.3	1292.7	1337.4	1288.6	-0.446	-0.235	-0.434	3.015	-0.745	0.005
0.1325	1318.7	1309.2	1316.3	1309.5	1358	1301.4	-0.72	-0.185	-0.696	2.981	-1.312	0.004
0.1921	1334.3	1323	1334.6	1323.4	1373.6	1312.4	-0.848	0.025	-0.817	2.943	-1.642	-0.001
0.2468	1348.3	1335.5	1352.2	1336	1386.8	1322.8	-0.949	0.289	-0.914	2.854	-1.895	-0.006
0.3319	1368	1354.7	1380.9	1355.3	1405.5	1339.4	-0.972	0.946	-0.931	2.745	-2.091	-0.019
0.4269	1389.3	1375.8	1415.3	1376.4	1424.4	1358.7	-0.973	1.871	-0.931	2.526	-2.2	-0.036
0.4858	1402.1	1388.7	1437.9	1389.2	1435.1	1371.2	-0.959	2.556	-0.917	2.355	-2.207	-0.049
0.5695	1420.3	1406.7	1472.1	1407.3	1449.2	1389.4	-0.957	3.644	-0.917	2.031	-2.176	-0.069
0.6412	1435.5	1421.9	1503.3	1422.5	1460	1405.6	-0.944	4.723	-0.908	1.709	-2.085	-0.088
0.7082	1449.4	1436	1534.4	1436.5	1469.3	1421.2	-0.924	5.863	-0.893	1.374	-1.946	-0.108
0.7729	1462.4	1449.4	1566.3	1449.8	1477.3	1436.7	-0.888	7.104	-0.863	1.016	-1.755	-0.128
0.8415	1474.9	1463.4	1602.4	1463.7	1484.5	1453.7	-0.776	8.644	-0.758	0.648	-1.435	-0.153
0.9069	1485.4	1476.7	1639.3	1476.8	1490	1470.5	-0.588	10.358	-0.577	0.311	-1.006	-0.179
1	1495.2	1495.2	1696.4	1495.2	1495.2	1495.2	0	13.456	0	0	0	-0.223
308.15 H	ζ											
0	1258.5	1258.5	1258	1258.5	1258.5	1258.5	-1.526	-1.565	-1.525	-1.526	-1.526	0.032
0.0612	1278.3	1273.3	1264.2	1273.5	1280.8	1269.3	-1.499	-2.203	-1.481	-0.916	-1.811	0.046
0.1325	1299	1290.3	1272.3	1290.8	1304.5	1282.2	-1.465	-2.842	-1.432	-0.386	-2.086	0.059
0.1921	1314.8	1304.4	1279.8	1305	1322.6	1293.4	-1.436	-3.291	-1.392	-0.059	-2.269	0.069
0.2468	1328.6	1317.2	1287.4	1317.8	1338.2	1303.9	-1.408	-3.635	-1.357	0.164	-2.402	0.077
0.3319	1348.9	1336.8	1300.5	1337.6	1360.6	1320.8	-1.363	-4.039	-1.305	0.395	-2.542	0.086
0.4269	1370.8	1358.3	1317.2	1359.2	1383.7	1340.5	-1.312	-4.3	-1.25	0.53	-2.604	0.092
0.4858	1384	1371.5	1328.7	1372.3	1397	1353.2	-1.279	-4.358	-1.218	0.56	-2.595	0.093
0.5695	1402.4	1389.9	1346.7	1390.8	1415	1371.8	-1.231	-4.301	-1.174	0.546	-2.518	0.092
0.6412	1418.1	1405.5	1363.9	1406.3	1429.3	1388.4	-1.189	-4.115	-1.137	0.483	-2.395	0.088
0.7082	1432.1	1419.9	1381.6	1420.6	1441.8	1404.4	-1.15	-3.821	-1.105	0.369	-2.232	0.081
0.7729	1444.8	1433.7	1400.2	1434.2	1452.8	1420.4	-1.112	-3.421	-1.074	0.208	-2.03	0.072
0.8415	1457.4	1448	1421.8	1448.5	1463.2	1437.8	-1.071	-2.862	-1.044	-0.034	-1.769	0.06
0.9069	1468.1	1461.6	1444.5	1461.8	1471.6	1455.1	-1.032	-2.19	-1.015	-0.351	-1.474	0.045
1	1480.6	1480.6	1480.6	1480.6	1480.6	1480.6	-0.977	-0.977	-0.976	-0.977	-0.977	0.02

303.15 K

Table 1. N-Ethylaniline +Toluene

 Table 2. N-Ethylaniline + o-Nitrotoluene

303.15 K

x1	u/exp	Unomoto	Uimx	Uir	Urao	Uj	%Unom	%Uimx	%Uir	%Ur	%Uj	α
0	2103	2103	2103	2103	2013	2103	0	0	0	-4.28	0	0
0.0745	2063.2	2049.7	2021	2065.1	1969.1	2009.5	-0.654	-2.472	0.092	-4.562	-2.604	0.051
0.1642	2015.5	1987.4	1935.6	2018.1	1917.8	1916.1	-1.392	-4.885	0.13	-4.846	-4.934	0.105
0.2205	1985.5	1949.4	1888.2	1987.9	1886.4	1865.8	-1.818	-6.13	0.119	-4.991	-6.03	0.135
0.2925	1945.6	1901.9	1833.2	1948.3	1847	1809	-2.248	-7.393	0.137	-5.07	-7.022	0.166
0.3705	1902.5	1851.8	1779.9	1904.2	1805	1755.3	-2.666	-8.485	0.087	-5.123	-7.737	0.194
0.4325	1865.7	1813	1741.4	1868.2	1772.2	1717.5	-2.827	-9.044	0.132	-5.01	-7.944	0.209
0.5124	1816.2	1764.2	1696.1	1820.5	1730.6	1674.1	-2.863	-9.437	0.239	-4.711	-7.826	0.219
0.5825	1771.5	1722.6	1660	1777.6	1694.8	1640.2	-2.762	-9.524	0.342	-4.332	-7.413	0.222
0.6612	1720.2	16/7.1	1622.9	1/2/.9	1655.2	1606.1	-2.507	-9.357	0.446	-3.778	-6.633	0.217
0.7402	1667.7	1632.7	1588.9	1676.4	1616.3	1575.5	-2.101	-8.922	0.524	-3.081	-5.527	0.206
0.8145	1618.2	1592	1559.5	1626.5	1580.5	1549.7	-1.616	-8.311	0.516	-2.329	-4.235	0.189
0.8852	1570.2	1554.4	1533.5	1577.7	1547.3	1527.3	-1.008	-7.503	0.476	-1.458	-2.729	0.169
0.9124	1552.9	1540.1	1524	1558.5	1534.7	1519.3	-0.822	-7.215	0.36	-1.17	-2.164	0.162
1	1495.2	1495.2	1495.2	1495.2	1495.2	1495.2	0	-5.999	0	0	0	0.132
308.15 K												
0	2093	2093	2093	2093	2093	2093	0.0001	0	0	-0.0001	0	0
0.0745	2063.1	2039.2	2009.8	2054.9	2040.1	1997.9	-1.1607	-2.583	-0.399	-1.1155	-3.1596	0.0537
0.1642	2016.5	1976.3	1923.4	2007.6	1978.1	1903.2	-1.9946	-4.6145	-0.4415	-1.9026	-5.6163	0.0991
0.2205	1988.5	1937.9	1875.5	1977.1	1940.2	1852.4	-2.5457	-5.6817	-0.5714	-2.4284	-6.8431	0.1241
0.2925	1946.7	1889.9	1820.1	1937.3	1892.7	1795.1	-2.9164	-6.5045	-0.4847	-2.7744	-7.786	0.144
0.3705	1900.4	1839.4	1766.3	1892.9	1842.5	1741.1	-3.2095	-7.0557	-0.3971	-3.0474	-8.3829	0.1576
0.4325	1861.4	1800.3	1727.6	1856.6	1803.5	1703.1	-3.2837	-7.1898	-0.257	-3.1116	-8.5056	0.1609
0.5124	1809.3	1751.2	1682.1	1808.6	1754.3	1659.5	-3.2137	-7.0299	-0.0364	-3.0379	-8.2803	0.1569
0.5825	1762.8	1709.2	1645.8	1765.3	1712.2	1625.5	-3.039	-6.6355	0.143	-2.8676	-7.7889	0.1472
0.6612	1710.4	1663.4	1608.6	1715.3	1666.2	1591.4	-2.7463	-5.9526	0.2837	-2.5861	-6.9592	0.1306
0.7402	1657.1	1618.8	1574.4	1663.4	1621.1	1560.8	-2.3137	-4.9877	0.38	-2.1747	-5.8114	0.1077
0.8145	1606.4	1577.9	1545	1613.1	1579.7	1535	-1.7737	-3.8252	0.4172	-1.6632	-4.4473	0.0811
0.8852	1559.1	1540	1519	1563.8	1541.2	1512.7	-1.2221	-2.5738	0.3017	-1.1471	-2.9782	0.0535
0.9124	1540.4	1525.7	1509.5	1544.5	1526.6	1504.6	-0.9519	-2.0077	0.263	-0.8935	-2.322	0.0414
1	1480.6	1480.6	1480.6	1480.6	1480.6	1480.6	0	0	0.0004	0.0001	0.0002	0

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 Table 3. N-Ethylaniline + m-Nitrotoluene

303	.15	K
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0.8415 0.9069

1

1.0208

1.0123

1

1.0268

1.0156

1

0.8852

0.9124

1

1.032

1.024

1

x1	u/exp l	Unomoto	) Uimx	Uir	Urao	Uj	%Unon	n%Uimx	%Uir	%Ur	%Uj	α
0	2087	2087	2087	2087	2087	2087	0	0	0	0	0	0
0.0805	2043.3	2031.4	2002	2046.9	2030	1991.1	-0.584	-2.021	0.176	-0.651	-2.555	0.042
0.1568	2001	1980.1	1931.7	2007.9	1978.4	1914.6	-1.047	-3.462	0.343	-1.127	-4.319	0.073
0.2258	1962.4	1934.8	1875.2	1971.6	1933.5	1854.8	-1.405	-4.443	0.471	-1.472	-5.481	0.095
0.2874	1927.9	1895.4	1829.5	1938.6	1894.4	1807.7	-1.688	-5.102	0.553	-1.735	-6.234	0.11
0.3625	1885.3	1848.4	1779.1	1897.2	1848	1756.8	-1.958	-5.635	0.632	-1.978	-6.816	0.123
0.4405	1840.3	1800.9	1731.8	1853.1	1800.9	1710.3	-2.142	-5.895	0.695	-2.143	-7.066	0.129
0.5101	1799.8	1759.6	1693.5	1812.6	1759.6	1673.3	-2.236	-5.907	0.712	-2.234	-7.026	0.13
0.5825	1756.7	1717.6	1656.9	1769.4	1717.6	1638.9	-2.225	-5.679	0.723	-2.228	-6.708	0.124
0.6635	1707 5	1671.9	1619.6	1719.6	1671.6	1604.3	-2.083	-5 148	0.71	-2.105	-6.042	0 111
0.7321	1665.2	1634.2	1590.5	1676.3	1633.6	1578	-1.86	-4.484	0.664	-1.897	-5.238	0.096
0 7956	1625.5	1600.1	1565 5	1635.1	1599.4	1555 7	-1 562	-3 692	0 588	-1 608	-4 295	0.078
0.8612	1584	1565.6	1541.3	1591.4	1564.9	1534 5	-1 159	-2.694	0.468	-1 204	-3 123	0.056
0.9212	1545.9	1534.8	1520.6	1550.5	1534.5	15167	-0 719	-1 637	0.297	-0 739	-1.89	0.034
1	1495.2	1495 2	1495 2	1495 2	1496.2	1495 2	0.717	0	0.277	0.067	0	0.054
308 15 K	1475.2	1475.2	1475.2	1475.2	1470.2	1475.2	0	0	0	0.007	0	
0	2080	2080	2080	2080	2080	2080	0 335	0 335	0 335	0 335	0 335	0.007
0.0805	2080	2080	1003.2	2080	2080	1082.1	-0.333	-0.555	-0.333	-0.333	-0.555	0.007
0.0005	2041.2	1071 5	1021.6	1000.0	1070.8	1004.2	1 811	4 205	0.307	1 8/7	5 163	0.000
0.1508	1068.0	1971.5	1921.0	1999.9	1970.8	1904.2	2 3 3 4	-4.295	0.399	2 3 5 5	-5.105	0.092
0.2238	1025.0	1925.0	1004.2	1020.7	1925.2	1705 7	2.334	6 226	0.429	2.333	7 267	0.117
0.2674	1955.9	1005.0	1017.9	1929.7	1005.5	1744.0	2 1 2 2	-0.220	-0.436	-2.739	-7.307	0.157
0.3023	1895.4	1000	1718.0	100/.0	1000.2	1/44.2	-3.122	-0.8/9	-0.490	-3.111	-8.003	0.155
0.4403	1840.7	1749.9	1/10.9	1845.1	17490.2	1697.2	-5.412	-7.24	-0.338	-3.392	-0.415	0.162
0.5101	1803.2	1/48	1680.2	1802.1	1/48.3	1659.9	-3.303	-7.305	-0.579	-3.548	-8.425	0.164
0.5825	1/5/.1	1/05.5	1643.4	1/58.4	1/05./	1625.1	-3.609	-7.124	-0.625	-3.603	-8.154	0.159
0.0035	1/04.5	1009.0	1605.7	1/0/.9	1639	1590.5	-3.508	-0.025	-0.08	-3.525	-/.518	0.147
0.7321	1658.9	1621.1	15/6.4	1664	1620.5	1563.8	-3.287	-5.955	-0./31	-3.324	-6./0/	0.131
0.7956	1616.8	1586.6	1551.2	1622.3	1585.8	1541.4	-2.962	-5.12/	-0.782	-3.015	-5.729	0.111
0.8612	15/3./	1551.8	1526.9	15/8.1	1550.8	1520.1	-2.49	-4.051	-0.839	-2.553	-4.48	0.086
0.9212	1534.5	1520.6	1506.1	1536.6	1519.8	1502.2	-1.928	-2.862	-0.895	-1.98	-3.115	0.06
1	1480.6	1480.6	1480.6	1480.6	1480.6	1480.6	-0.977	-0.977	-0.976	-0.977	-0.976	0.02
Table 4	<b>1.</b> $U^2/U^2$	_{imix} valu	es for al	l three s	ystems	studied	at temp	eratures	303.1	5 K and	308.15	κ
EA+	toluene	e		E	A+o-N	itrotolu	lene		EA+	<i>m</i> -Nitr	otoluen	e
x1	303.1	5 K 30	)8.15 K	x1	303.	15 K	308.15	Кx	:1	303.15	K 30	8.15 K
0	1		1	0		1	1		0	1		1
0.0612	2 1.00	96 1	.0122	0.074	5 1.0	)18	1.027	0.0	805	1.042	2 1	.055
0.1325	5 1.01	99 1	.0278	0.164	2 1.0	)49	1.064	0.1	568	1.073	31	.092
0.1921	1.02	66 1	.0376	0.220	5 1.0	)71	1.088	0.2	258	1.095	51	.119
0.2468	3 1.03	27 1	.0431	0.292	5 1.0	)86	1.106	0.2	874	1.11	1	.137
0.3319	1.03	85	1.051	0.370	5 1.0	)99	1.122	0.3	625	1.123	31	.153
0.4269	0 1.04	43 1	.0558	0.432	5 1.1	05	1.131	0.4	405	1.129	) 1	.162
0.4858	3 1.04	41 1	.0588	0.512	4 1.1	06	1.133	0.5	101	1.13	1	.164
0.5695	5 1.04	35 1	.0579	0.582	5 1	.1	1.128	0.5	825	1.124	4 1	.159
0.6412	2 1.04	09	1.054	0.661	2 1.0	)87	1.116	0.6	635	1.111	l 1	.147
0.7082	2 1.03	67 1	.0483	0.740	2 1.0	)72	1.1	0.7	321	1.096	51	.131
0.7729	0 1.02	95 1	.0384	0.814	5 1.0	)54	1.08	0.7	956	1.078	31	.111

1.055 1.039

1

0.8612 0.9212

1

1.056

1.034

1

1.086

1.06

1



Figures 1-3 represent the variation of  $U^2_{exp}$  /  $U^2_{imix}$  with mole fraction of ethyl aniline

**Figures 1-3.** Plots of  $U_{exp}^2 / U_{imix}^2$  for the studied systems at temperatures 303.15 K and 308.15 K

The interaction parameter characterizing a system varies with the composition, molar mass and temperature. It is employed to account for the contribution of non-combinatorial entropy of mixing and the enthalpy of mixing to the Gibb's energy of mixing. A positive value of  $\alpha$  in all the system clearly indicates the existence of strong tendency for the formation of association in mixture through dipole-dipole interactions higher values of percentage deviation indicates maximum departure of the particular theory from experiment at that particular concentration. In systems studied, we observed that the interaction parameters are having a very low magnitude for all the given mixtures, indicating moderate/ weaker interactions, though hydrogen bonding, which decreases from *o*-nitro toluene to m-nitro toluene.

The deviations between theoretical and experimental value of ultrasonic velocities decrease with increase of temperature due to breaking of hetero and homo molecular clusters at higher temperatures²⁷. On increasing the temperature, the ultrasonic velocity values decrease in the three binary liquid mixtures. This is probably may be due to the fact that the thermal energy activates the molecule, which would increase the rate of association of unlike molecules.

On the whole, all the theoretical models fairly predicted ultrasonic velocities, are reasonably close to the experimental values for and the three binary mixtures reported in this work, thus showing the validity of studied theoretical models for binary mixtures. The predictive abilities of various ultrasonic theories discussed above, depend upon the strength interaction prevailing in a system²⁸.

# Conclusion

The application of various ultrasonic velocity theories have been studied with binary mixtures of *N*-ethyl aniline with toluene *o*-nitro toluene and *m*-nitrotoluene. It may be concluded that out of five theories and relations discussed above the Nomoto's relation, Van Deal ideal mixing relation and Impedance relation provided good results. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by NomotoVan Dael and Vangeel and Impedance relation, in deriving the empirical relations have been truly observed in the studied binary liquid mixtures.

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