Available online at www.elixirpublishers.com (Elixir International Journal)

Ultrasonics

Elixir Ultrasonics 65 (2013) 19808-19814

ISSN: 2229-712X

Application of various theories of ultrasonic velocities in binary liquid mixtures of N-ethylaniline with some organic compounds

B.Jhansi Lakshmi[1], M. Gowri Sankar[2], Zareena Begum[1], D.Ramachandran[1] and C.Rambabu[1,*]

[1]Department of Chemistry, Acharya Nagarjuna University, A.P, India.

[2]Department of Chemistry, J.K.C College, Guntur, A.P, India.

ARTICLE INFO

Article history:

Received: 4 October 2013;

Received in revised form:

25 November 2013;

Accepted: 5 December 2013;

Keywords

Theoretical velocities,

Ultrasonics,

Hydrogen bonding,

Interaction parameter.

ABSTRACT

Ultrasonic velocities and densities of the binary liquid mixtures of N-ethylaniline with five different organic compounds like chlorobenzene, bromobenzene, 1,2,dichlorobenzene, 1,3,dichlorobenzene and 1,2,4 trichlorobenzene have been measured at temperatures 303.15 and 308.15K.over the entire composition range. The theoretical values of ultrasonic velocity were applied in evaluating the velocities using the Nomoto's relation(U_{NR}), Impedence relation(U_{IR}), Ideal mixing relation(U_{IMR}) , Jungie's relation(U_{JR})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.

Introduction

In recent years measurement of ultrasonic investigations find extensive applications in determining the Physico-chemical behavior of liquid mixtures [1-5]. Several researchers [6-9]. carried out ultrasonic investigations and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto[10] , Van Deal and Vangeel ideal mix relations [11] impedance relation [12] Rao's Specific velocity [13] and Junjie [14] and interpreted the results in terms of molecular interactions. ultrasonic study of liquid mixtures, due to its non destructive nature, have 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 Correy [15] discussed sound velocity in a liquid as the sum of bond velocities. Randall [16] 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 Younglove [21] 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 Ethylaniline and chlorobenzene, bromobenzene, 1,2,dichlorobenzene, 1,3,dichlorobenzene and 1,2,4 trichlorobenzene at temperatures 303.15 and 308.15K ,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]

Ethlyaniline (Merck India >0.995 purity) was distilled at low pressure and over freshly activated 0.3 nm molecular sieves [24] Other compounds under study as mentioned above (SD Fine Chemicals, India, with purity >0.995) were purified by methods described in the literature [25] 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) is measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi model - F05) operating at 2 MHz. with a precision of 0.8 $m.sec^{-1}$ and an uncertainty less than ± 0.1$m.sec^{-1}$. The temperature stability was maintained within±0.01K by circulating water bath around the measuring cell through a pump.

The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built- in solid-state thermostat and a resident program with accuracy of temperature of 303.15 K ± 0.03 K. The values from triplicate replication at each temperature are reproducible within 2 x 10^{-1} kg m^3 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

Tele:

E-mail addresses: rbchintala@gmal.com

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

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

$M = (X_1M_1 + X_2M_2)$ ..... (2)

where M_1 and M_2 are molecular weights of constituent components.

Simple manipulation yields the following relation4

$U_{NR} = [(X_1R_1+X_2R_2) / (X_1V_1+X_2V_2)]^3$ ..... (3)

The 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 relation is given as

$U_{IR} = \Sigma X_i Z_i / \Sigma X_i\rho_i$ ....(4)

where X_i mole fraction, ρ_{t} is the density of the mixture and Z_i is the acoustic impedance

The Jungie equation (U_J)

The Junjie equation is given as

$U_J = (X_1M_1/\rho_1+X_2M_2/\rho_2)/ [\{X_1M_1+X_2M_2\}^{1/2} \{X_1M_1/\rho_1U_1^2+X_2M_2/\rho_2U_2^2)\}^{1/2}]$ .....(5)

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

The Rao's specific velocity method relation (U_R):

Rao's specific velocity method[11] $U_R = (\Sigma X_i r_i d)^3$ ……..(6)

where Xi is the mole fraction, U_i the ultrasonic velocity and ρ_{t} 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

$1/(X_1M_1+X_2M_2)*1/U^2_{imix} = X_1/M_1U_1^2+X_2/M_2U_2^2$ …….. (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)

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

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

Results and discussions:

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. The presence of an amine group strongly increases the reactivity of the aromatic ring, due to an electron-donating effect.

When a halogen atom is introduced into the aromatic ring, it causes to change in the π- electron density around the aromatic ring because of positive mesomeric and positive electromeric effects. (+T effect > -I effect). Further, substitution of second and third chloro groups in benzene molecule increase the distance of closest approach of the N-ethylaniline and dichloro, trichlorobenzene molecule resulting decrease is interaction between component molecules. The effect on the π-electron density due to increase in the number of chlorine atoms from chlorobenzene to di/trichlorobenzene is relatively small, which tend to decrease the magnitude of V^E. The difference in shapes of molecules with the addition of chloro groups also leads to different alignments in the liquid mixtures. Further, the electron donor-acceptor interactions tend to decrease with addition of chloro 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 303.15-318.15K. 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 Dependence 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 are observed.

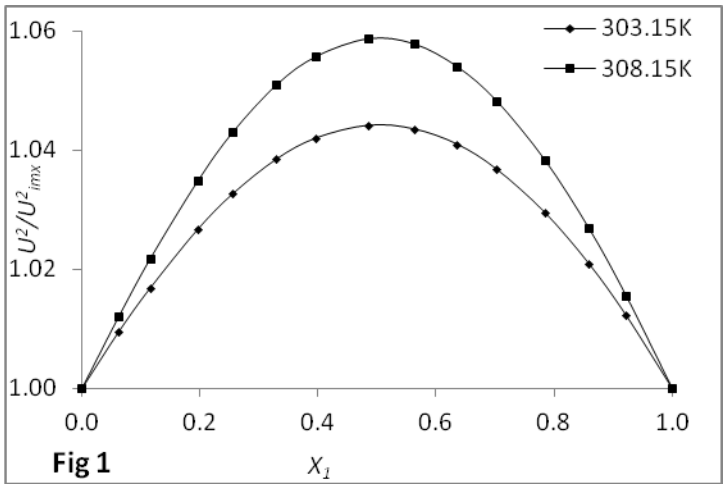
Data reveal that the sound speed computed from impedance relation,U_{IR} exhibit more satisfactory agreement with the experimental values in the temperature range 303.15K-318.15K than other approaches in the binary systems N-ethylaniline + chlorobenzene, + bromobenzene,

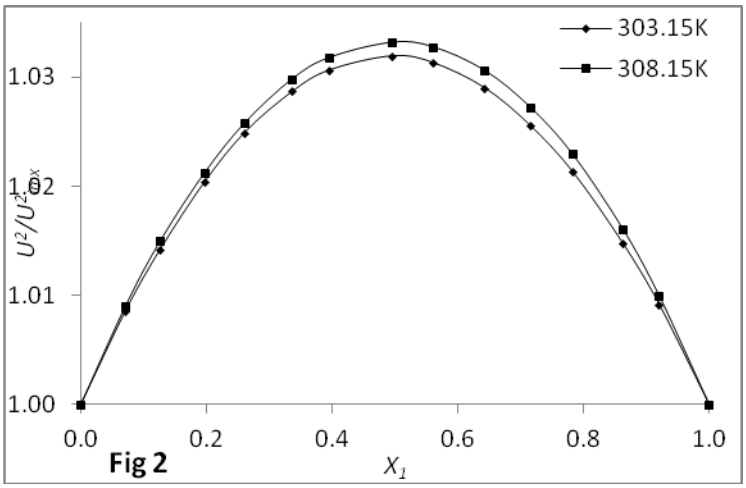
Table 1 shows that in the system of N-ethylaniline + chlorobenzene, there is good agreement between experimental and theoretical values calculated by impedance and Nomoto relations. Here Nomoto relation provides the best result than the Impedance relation at all the temperatures. However, higher deviations are observed in Rao's specific and slight variations in Junjie's theories.

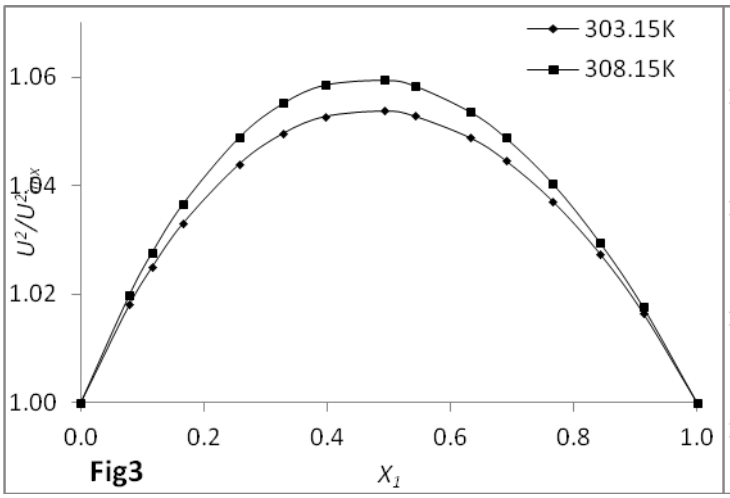
Ethylaniline+ bromobenzene, system, as described in Table 2, there is good agreement between experimental and theoretical values in Nomoto relation followed by impedance relations where as higher deviations are observed in VanDael ideal mixing relation, Rao's specific velocity method and Junjie's relation.

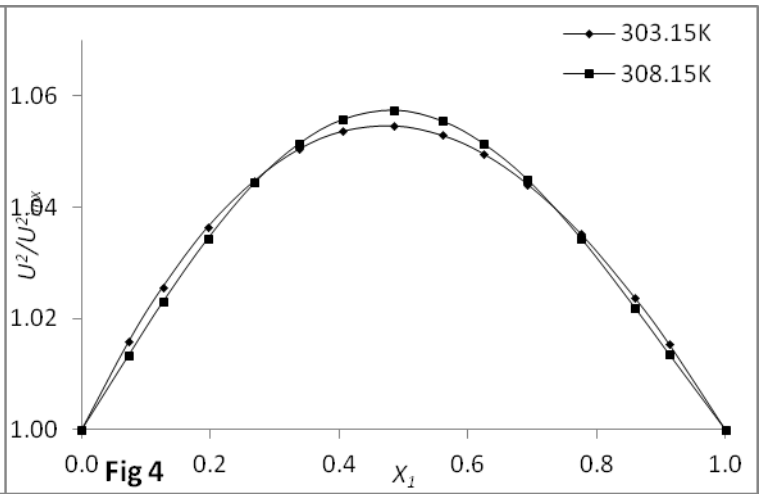
Ethylaniline and 1, 2-dichlorobenzene, + 1, 3-dichlorobenzene, +1, 2, 4-trichlorobenzene showed good agreement between experimental and theoretical values calculated by Rao's specific velocity method and impedance relation. Here Rao's specific velocity method provides the best result than the result of impedance relation at all temperatures. However, higher deviations are observed in Nomoto's relation, Van Dael ideal mixing relation and Junjie's theory. Tables 3-5 show the derived velocity values for these systems.

Figures 1-5: Plots of U^2/U^2_{imix} for the studied systems at temperatures 303.15K and 308.15K. (ethylaniline+chlorobenzene(figure1) ethylaniline + bromobenzene (fig.2) ethylaniline +1,2 di chloro benzene(fig 3); ethylaniline +1,3 di chlorobenzene(fig 4); ethylaniline +1,2,4 trichlorobenzene(fig 5)









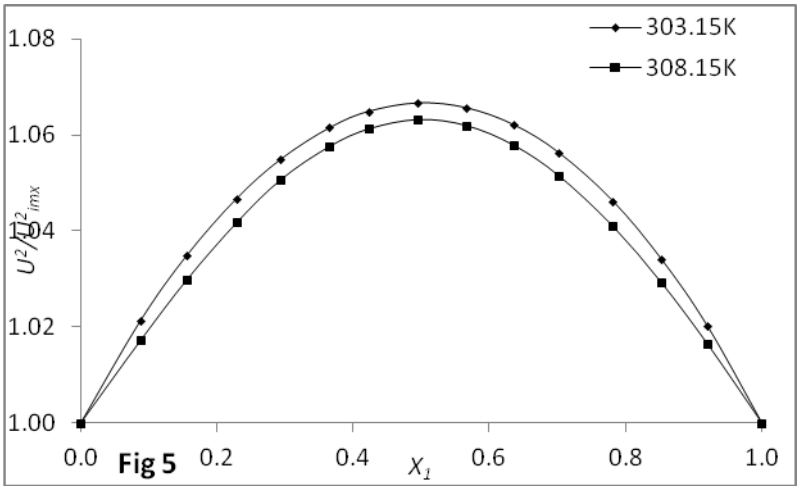


Table 1: Ethylaniline + chlorobenzene at 303.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_i	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_i$	α
0.0000	1251.00	1251.00	1251.00	1251.00	1251.00	1251.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0629	1268.00	1268.72	1261.96	1264.47	1269.80	1266.82	0.0567	-0.4766	-0.2782	0.1421	-0.0934	0.0096
0.1159	1282.20	1283.37	1271.52	1276.00	1283.92	1280.09	0.0913	-0.8326	-0.4839	0.1338	-0.1644	0.0169
0.1959	1303.60	1305.02	1286.58	1293.70	1303.81	1300.05	0.1088	-1.3056	-0.7596	0.0162	-0.2725	0.0266
0.2558	1319.40	1320.87	1298.37	1307.20	1318.49	1314.92	0.1115	-1.5941	-0.9245	-0.0692	-0.3394	0.0327
0.3298	1338.60	1340.04	1313.58	1324.19	1336.38	1333.22	0.1079	-1.8692	-1.0765	-0.1662	-0.4019	0.0385
0.3968	1355.60	1357.02	1328.01	1339.87	1352.68	1349.72	0.1051	-2.0351	-1.1604	-0.2156	-0.4341	0.0420
0.4856	1377.60	1378.99	1348.18	1361.10	1374.09	1371.47	0.1009	-2.1352	-1.1977	-0.2545	-0.4450	0.0441
0.5625	1396.10	1397.53	1366.70	1379.91	1392.79	1390.21	0.1025	-2.1061	-1.1594	-0.2371	-0.4217	0.0435
0.6359	1413.40	1414.83	1385.35	1398.26	1410.60	1408.02	0.1009	-1.9848	-1.0715	-0.1979	-0.3806	0.0409
0.7025	1428.70	1430.19	1403.17	1415.23	1426.68	1424.11	0.1043	-1.7871	-0.9427	-0.1414	-0.3212	0.0367
0.7839	1447.10	1448.55	1426.21	1436.43	1446.44	1443.69	0.1004	-1.4435	-0.7376	-0.0454	-0.2358	0.0295
0.8592	1463.90	1465.15	1448.88	1456.48	1464.32	1461.71	0.0852	-1.0261	-0.5066	0.0284	-0.1495	0.0208
0.9215	1477.70	1478.60	1468.70	1473.42	1478.48	1476.56	0.0609	-0.6088	-0.2898	0.0530	-0.0769	0.0123
1.0000	1495.20	1495.20	1495.20	1495.20	1495.20	1495.20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Ethyl aniline + chlorobenzene at 308.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_i	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_i$	α
0.0000	1225.20	1225.20	1225.20	1225.20	1225.20	1225.20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0629	1244.00	1243.62	1236.49	1239.32	1244.28	1241.49	-0.0306	-0.6033	-0.3764	0.0224	-0.2019	0.0122
0.1159	1259.90	1258.86	1246.37	1251.40	1259.13	1255.19	-0.0822	-1.0740	-0.6749	-0.0609	-0.3740	0.0218
0.1959	1283.70	1281.41	1261.93	1269.95	1280.43	1275.82	-0.1782	-1.6959	-1.0714	-0.2543	-0.6136	0.0348
0.2558	1301.30	1297.94	1274.13	1284.09	1295.97	1291.24	-0.2582	-2.0878	-1.3223	-0.4099	-0.7731	0.0431
0.3298	1322.40	1317.95	1289.90	1301.88	1314.78	1310.25	-0.3365	-2.4575	-1.5515	-0.5760	-0.9190	0.0510
0.3968	1340.80	1335.69	1304.89	1318.30	1331.81	1327.42	-0.3813	-2.6780	-1.6784	-0.6704	-0.9979	0.0558
0.4856	1364.30	1358.66	1325.89	1340.51	1354.34	1350.13	-0.4137	-2.8152	-1.7436	-0.7303	-1.0387	0.0588
0.5625	1383.60	1378.06	1345.21	1360.19	1373.74	1369.75	-0.4001	-2.7748	-1.6919	-0.7127	-1.0011	0.0579
0.6359	1401.10	1396.18	1364.71	1379.37	1392.64	1388.44	-0.3509	-2.5970	-1.5511	-0.6037	-0.9038	0.0540
0.7025	1416.40	1412.29	1383.40	1397.11	1409.74	1405.36	-0.2900	-2.3301	-1.3618	-0.4700	-0.7794	0.0483
0.7839	1434.40	1431.56	1407.62	1419.25	1430.33	1426.00	-0.1977	-1.8669	-1.0560	-0.2835	-0.5853	0.0384
0.8592	1450.60	1448.99	1431.52	1440.20	1449.09	1445.06	-0.1107	-1.3152	-0.7171	-0.1044	-0.3818	0.0268
0.9215	1463.80	1463.13	1452.49	1457.87	1463.68	1460.80	-0.0455	-0.7728	-0.4049	-0.0080	-0.2048	0.0156
1.0000	1480.60	1480.60	1480.60	1480.61	1480.60	1480.60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 2: Ethylaniline + bromobenzene at 303.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_i	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_i$	α
0.0000	1135.40	1135.40	1135.40	1135.40	1135.40	1135.40	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0714	1160.20	1163.28	1155.24	1152.35	1202.44	1157.98	0.2656	-0.4274	-0.6765	3.6407	-0.1913	0.0086
0.1264	1179.30	1184.52	1171.00	1166.03	1250.19	1175.64	0.4430	-0.7034	-1.1254	6.0114	-0.3102	0.0142
0.1965	1203.80	1211.31	1191.73	1184.30	1305.81	1198.50	0.6236	-1.0025	-1.6202	8.4742	-0.4399	0.0204
0.2605	1226.30	1235.47	1211.31	1201.85	1351.18	1219.74	0.7479	-1.2226	-1.9935	10.1836	-0.5353	0.0249
0.3365	1253.00	1263.81	1235.41	1223.89	1398.34	1245.41	0.8629	-1.4041	-2.3233	11.5997	-0.6058	0.0287
0.3956	1273.90	1285.58	1254.82	1241.99	1429.94	1265.74	0.9172	-1.4977	-2.5053	12.2491	-0.6407	0.0306
0.4958	1309.60	1321.97	1289.17	1274.79	1472.99	1300.97	0.9446	-1.5599	-2.6583	12.4766	-0.6592	0.0319
0.5606	1332.80	1345.15	1312.41	1297.56	1493.91	1324.29	0.9266	-1.5300	-2.6440	12.0882	-0.6388	0.0313
0.6429	1362.50	1374.19	1343.16	1328.46	1512.67	1354.54	0.8583	-1.4197	-2.4986	11.0219	-0.5839	0.0290
0.7152	1388.80	1399.35	1371.39	1357.61	1522.03	1381.75	0.7595	-1.2539	-2.2459	9.5928	-0.5077	0.0256
0.7825	1413.60	1422.46	1398.75	1386.62	1524.57	1407.62	0.6268	-1.0503	-1.9085	7.8504	-0.4227	0.0213
0.8628	1443.40	1449.66	1432.87	1423.87	1520.52	1439.23	0.4338	-0.7293	-1.3528	5.3431	-0.2890	0.0147
0.9205	1465.10	1468.96	1458.44	1452.60	1512.54	1462.45	0.2633	-0.4546	-0.8529	3.2379	-0.1806	0.0092
1.0000	1495.20	1495.20	1495.20	1495.20	1495.20	1495.20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Ethylaniline + bromobenzene at 308.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_i	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_i$	α
0.0000	1124.60	1124.60	1124.60	1124.60	1124.60	1124.60	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
0.0714	1149.40	1151.16	1144.24	1142.04	1187.16	1146.51	0.1533	-0.4492	-0.6406	3.2853	-0.2516	0.0090
0.1264	1168.50	1171.51	1159.84	1156.06	1231.83	1163.69	0.2579	-0.7414	-1.0649	5.4200	-0.4115	0.0150
0.1965	1192.80	1197.31	1180.35	1174.71	1284.11	1185.99	0.3780	-1.0438	-1.5163	7.6550	-0.5705	0.0212
0.2605	1215.10	1220.72	1199.72	1192.57	1327.08	1206.77	0.4622	-1.2656	-1.8539	9.2159	-0.6859	0.0258
0.3365	1241.70	1248.33	1223.57	1214.88	1372.18	1231.96	0.5341	-1.4602	-2.1598	10.5084	-0.7847	0.0299
0.3956	1262.40	1269.67	1242.78	1233.12	1402.75	1251.96	0.5757	-1.5541	-2.3193	11.1179	-0.8272	0.0318
0.4958	1297.80	1305.56	1276.77	1265.99	1445.23	1286.73	0.5980	-1.6204	-2.4514	11.3597	-0.8532	0.0332
0.5606	1320.90	1328.58	1299.76	1288.66	1466.46	1309.82	0.5815	-1.6003	-2.4407	11.0194	-0.8392	0.0328
0.6429	1350.40	1357.60	1330.19	1319.23	1486.37	1339.86	0.5331	-1.4969	-2.3079	10.0687	-0.7807	0.0306

0.7152	1376.50	1382.89	1358.12	1347.89	1497.34	1366.94	0.4639	-1.3356	-2.0788	8.7789	-0.6943	0.0273
0.7825	1401.00	1406.25	1385.19	1376.21	1501.77	1392.77	0.3747	-1.1284	-1.7692	7.1925	-0.5876	0.0230
0.8628	1430.30	1433.91	1418.95	1412.31	1500.49	1424.39	0.2522	-0.7938	-1.2575	4.9072	-0.4131	0.0161
0.9205	1451.40	1453.63	1444.24	1439.95	1494.69	1447.69	0.1537	-0.4936	-0.7888	2.9826	-0.2559	0.0099
1.0000	1480.60	1480.60	1480.60	1480.61	1480.60	1480.60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 3: Ethylaniline + 1, 2 di chlorobenzene at 303.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_j	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_j$	α
0.0000	1266.00	1266.0	1266.00	1266.00	1266.00	1266.00	-0.0003	0.0000	0.0000	0.0000	0.0000	0.0000
0.0789	1293.00	1285.1	1281.47	1279.55	1304.66	1282.35	-0.6097	-0.8917	-1.0404	0.9016	-0.8235	0.0181
0.1156	1304.80	1293.9	1288.80	1286.05	1321.46	1290.05	-0.8316	-1.2265	-1.4371	1.2772	-1.1308	0.0250
0.1659	1320.30	1306.0	1298.98	1295.18	1343.26	1300.68	-1.0838	-1.6149	-1.9029	1.7390	-1.4860	0.0331
0.2569	1346.50	1327.6	1317.82	1312.36	1379.09	1320.20	-1.4043	-2.1302	-2.5358	2.4205	-1.9532	0.0440
0.3287	1365.80	1344.5	1333.07	1326.56	1404.03	1335.86	-1.5621	-2.3961	-2.8733	2.7991	-2.1919	0.0497
0.3968	1383.00	1360.3	1347.88	1340.59	1425.02	1350.94	-1.6390	-2.5393	-3.0668	3.0382	-2.3181	0.0528
0.4925	1405.60	1382.4	1369.26	1361.30	1450.08	1372.51	-1.6500	-2.5853	-3.1520	3.1645	-2.3543	0.0538
0.5421	1416.60	1393.7	1380.61	1372.51	1461.01	1383.87	-1.6132	-2.5403	-3.1121	3.1348	-2.3107	0.0528
0.6325	1435.60	1414.2	1401.80	1393.88	1477.30	1404.90	-1.4881	-2.3542	-2.9061	2.9048	-2.1386	0.0488
0.6897	1446.80	1427.1	1415.56	1408.05	1485.21	1418.43	-1.3628	-2.1595	-2.6782	2.6550	-1.9606	0.0446
0.7659	1460.70	1444.1	1434.31	1427.77	1492.83	1436.75	-1.1395	-1.8069	-2.2541	2.1996	-1.6395	0.0371
0.8425	1473.50	1461.0	1453.67	1448.64	1497.10	1455.51	-0.8513	-1.3458	-1.6870	1.6018	-1.2212	0.0275
0.9121	1483.90	1476.2	1471.73	1468.58	1498.05	1472.85	-0.5207	-0.8201	-1.0324	0.9538	-0.7444	0.0166
1.0000	1495.20	1495.2	1495.20	1495.20	1495.20	1495.20	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000

Ethylaniline + 1, 2 di chlorobenzene at 308.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_j	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_j$	α
0.0000	1251.00	1251.00	1251.00	1251.00	1251.00	1251.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0789	1279.00	1270.09	1266.47	1264.61	1289.93	1267.38	-0.6970	-0.9796	-1.1249	0.8547	-0.9086	0.0199
0.1156	1291.30	1278.91	1273.80	1271.14	1306.82	1275.08	-0.9599	-1.3552	-1.5609	1.2020	-1.2558	0.0277
0.1659	1307.30	1290.93	1283.99	1280.31	1328.47	1285.74	-1.2518	-1.7834	-2.0646	1.6194	-1.6494	0.0366
0.2569	1334.30	1312.52	1302.84	1297.56	1364.12	1305.29	-1.6320	-2.3581	-2.7538	2.2347	-2.1742	0.0489
0.3287	1354.00	1329.40	1318.11	1311.81	1388.83	1320.98	-1.8167	-2.6508	-3.1163	2.5725	-2.4387	0.0552
0.3968	1371.40	1345.28	1332.93	1325.88	1409.85	1336.08	-1.9045	-2.8051	-3.3193	2.8036	-2.5752	0.0586
0.4925	1394.00	1367.39	1354.34	1346.64	1434.88	1357.69	-1.9090	-2.8450	-3.3974	2.9325	-2.6048	0.0594
0.5421	1405.00	1378.75	1365.71	1357.88	1445.86	1369.07	-1.8683	-2.7963	-3.3535	2.9084	-2.5575	0.0584
0.6325	1423.60	1399.29	1386.94	1379.29	1462.32	1390.14	-1.7076	-2.5749	-3.1129	2.7201	-2.3506	0.0536
0.6897	1434.50	1412.18	1400.73	1393.47	1470.37	1403.70	-1.5562	-2.3544	-2.8600	2.5005	-2.1473	0.0488
0.7659	1447.90	1429.21	1419.52	1413.21	1478.27	1422.05	-1.2908	-1.9600	-2.3959	2.0975	-1.7855	0.0404
0.8425	1460.00	1446.18	1438.94	1434.08	1482.73	1440.83	-0.9465	-1.4426	-1.7753	1.5567	-1.3127	0.0295
0.9121	1469.90	1461.47	1457.05	1454.01	1483.67	1458.21	-0.5735	-0.8740	-1.0810	0.9369	-0.7950	0.0177
1.0000	1480.60	1480.60	1480.60	1480.61	1480.60	1480.60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4: Ethylaniline + 1, 3 dichlorobenzene at 303.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_j	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_j$	α
0.0000	1240.00	1240.00	1240.00	1240.00	1240.00	1240.00	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0725	1265.40	1259.13	1255.54	1254.06	1276.02	1256.62	-0.4953	-0.7796	-0.8958	0.8395	-0.6940	0.0158
0.1256	1283.30	1273.09	1267.16	1264.70	1300.71	1268.95	-0.7958	-1.2575	-1.4492	1.3567	-1.1180	0.0256
0.1956	1306.00	1291.40	1282.82	1279.19	1331.15	1285.43	-1.1175	-1.7746	-2.0530	1.9257	-1.5751	0.0365
0.2687	1328.40	1310.44	1299.60	1294.90	1360.23	1302.91	-1.3522	-2.1682	-2.5215	2.3959	-1.9192	0.0448
0.3369	1348.40	1328.10	1315.65	1310.14	1384.86	1319.47	-1.5053	-2.4290	-2.8372	2.7042	-2.1457	0.0504
0.4056	1367.50	1345.81	1332.22	1326.09	1407.25	1336.41	-1.5861	-2.5798	-3.0282	2.9071	-2.2735	0.0537
0.4856	1388.50	1366.32	1352.06	1345.46	1430.17	1356.48	-1.5977	-2.6247	-3.0999	3.0008	-2.3063	0.0546
0.5598	1406.80	1385.23	1370.99	1364.24	1448.37	1375.43	-1.5336	-2.5457	-3.0252	2.9551	-2.2301	0.0529
0.6235	1421.70	1401.37	1387.67	1381.04	1461.67	1391.96	-1.4297	-2.3937	-2.8600	2.8115	-2.0917	0.0497
0.6925	1436.90	1418.78	1406.20	1399.98	1473.62	1410.16	-1.2612	-2.1364	-2.5695	2.5558	-1.8607	0.0441
0.7759	1454.20	1439.69	1429.27	1423.97	1484.62	1432.58	-0.9978	-1.7140	-2.0785	2.0917	-1.4869	0.0352
0.8596	1470.30	1460.54	1453.21	1449.36	1491.84	1455.55	-0.6638	-1.1627	-1.4239	1.4647	-1.0034	0.0237
0.9125	1480.00	1473.65	1468.75	1466.14	1494.39	1470.32	-0.4293	-0.7603	-0.9368	0.9723	-0.6542	0.0154
1.0000	1495.20	1495.20	1495.20	1495.20	1495.20	1495.20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Ethylaniline + 1, 3 dichlorobenzene at 308.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_j	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_j$	α
0.0000	1229.00	1229.00	1229.00	1229.00	1229.00	1229.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0725	1252.60	1247.88	1244.33	1242.85	1264.97	1245.39	-0.3767	-0.6604	-0.7781	0.9875	-0.5754	0.0133
0.1256	1270.10	1261.65	1255.80	1253.34	1289.61	1257.56	-0.6654	-1.1259	-1.3198	1.5364	-0.9875	0.0229
0.1956	1292.90	1279.72	1271.25	1267.61	1319.89	1273.81	-1.0195	-1.6745	-1.9560	2.0876	-1.4767	0.0344
0.2687	1316.10	1298.49	1287.80	1283.10	1348.81	1291.04	-1.3379	-2.1506	-2.5074	2.4854	-1.9039	0.0444

0.3369	1336.70	1315.91	1303.63	1298.12	1373.24	1307.37	-1.5551	-2.4743	-2.8862	2.7334	-2.1939	0.0514
0.4056	1356.30	1333.37	1319.97	1313.84	1395.36	1324.08	-1.6903	-2.6785	-3.1308	2.8799	-2.3756	0.0558
0.4856	1377.50	1353.59	1339.53	1332.93	1417.99	1343.87	-1.7356	-2.7565	-3.2356	2.9393	-2.4417	0.0575
0.5598	1395.40	1372.23	1358.19	1351.45	1435.88	1362.55	-1.6603	-2.6663	-3.1497	2.9012	-2.3543	0.0555
0.6235	1409.60	1388.15	1374.64	1368.01	1448.90	1378.85	-1.5217	-2.4802	-2.9504	2.7881	-2.1815	0.0515
0.6925	1423.90	1405.30	1392.91	1386.69	1460.51	1396.79	-1.3061	-2.1766	-2.6136	2.5711	-1.9039	0.0450
0.7759	1439.80	1425.91	1415.65	1410.35	1471.09	1418.88	-0.9647	-1.6775	-2.0455	2.1732	-1.4528	0.0344
0.8596	1454.90	1446.45	1439.23	1435.39	1477.91	1441.52	-0.5806	-1.0772	-1.3411	1.5812	-0.9196	0.0219
0.9125	1464.40	1459.36	1454.54	1451.93	1480.19	1456.08	-0.3438	-0.6732	-0.8515	1.0779	-0.5682	0.0136
1.0000	1480.60	1480.60	1480.60	1480.61	1480.60	1480.60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 5: Ethylaniline + 1, 2, 4 tri chlorobenzene at 303.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_j	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_j$	α
0.0000	1257.00	1257.00	1257.00	1257.00	1257.00	1257.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0875	1285.90	1276.95	1272.43	1271.19	1335.88	1272.36	-0.6959	-1.0471	-1.1440	3.8865	-1.0526	0.0213
0.1559	1307.30	1292.67	1285.04	1282.90	1391.56	1284.93	-1.1195	-1.7025	-1.8663	6.4456	-1.7114	0.0349
0.2286	1329.00	1309.48	1299.00	1296.00	1444.30	1298.84	-1.4686	-2.2573	-2.4832	8.6759	-2.2691	0.0467
0.2938	1347.60	1324.66	1312.04	1308.35	1485.63	1311.85	-1.7020	-2.6389	-2.9124	10.2425	-2.6527	0.0549
0.3656	1367.20	1341.49	1327.00	1322.68	1523.56	1326.79	-1.8802	-2.9403	-3.2562	11.4368	-2.9556	0.0615
0.4225	1382.10	1354.91	1339.34	1334.61	1548.13	1339.11	-1.9671	-3.0941	-3.4357	12.0129	-3.1101	0.0649
0.4952	1400.20	1372.16	1355.75	1350.67	1571.95	1355.52	-2.0024	-3.1744	-3.5375	12.2659	-3.1906	0.0666
0.5659	1416.80	1389.05	1372.47	1367.22	1586.72	1372.25	-1.9585	-3.1288	-3.4994	11.9935	-3.1447	0.0656
0.6359	1432.30	1405.88	1389.81	1384.61	1593.06	1389.60	-1.8443	-2.9665	-3.3299	11.2241	-2.9814	0.0621
0.7025	1446.10	1422.00	1407.09	1402.15	1591.42	1406.89	-1.6665	-2.6976	-3.0389	10.0488	-2.7111	0.0562
0.7812	1461.20	1441.17	1428.57	1424.28	1579.83	1428.41	-1.3706	-2.2333	-2.5265	8.1189	-2.2444	0.0462
0.8525	1473.60	1458.66	1449.10	1445.77	1560.57	1448.98	-1.0137	-1.6628	-1.8889	5.9017	-1.6709	0.0341
0.9199	1484.30	1475.30	1469.52	1467.46	1534.79	1469.45	-0.6064	-0.9956	-1.1343	3.4016	-1.0003	0.0202
1.0000	1495.20	1495.20	1495.20	1495.20	1495.20	1495.20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Ethyl aniline + 1, 2, 4 trichlorobenzene at 308.15K

X_1	U_{expt}	U_{Nom}	U_{imx}	U_{ir}	U_{rao}	U_j	$\%U_{Nom}$	$\%U_{imx}$	$\%U_{ir}$	$\%U_{rao}$	$\%U_j$	α
0.0000	1248.00	1248.00	1248.00	1248.00	1248.00	1248.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0875	1273.80	1267.51	1263.02	1261.85	1327.12	1262.94	-0.4940	-0.8465	-0.9384	4.1855	-0.8528	0.0171
0.1559	1294.20	1282.87	1275.29	1273.28	1382.53	1275.16	-0.8755	-1.4609	-1.6166	6.8254	-1.4712	0.0299
0.2286	1315.50	1299.31	1288.89	1286.06	1434.66	1288.71	-1.2310	-2.0228	-2.2379	9.0585	-2.0365	0.0417
0.2938	1334.20	1314.14	1301.60	1298.12	1475.09	1301.38	-1.5033	-2.4436	-2.7042	10.5597	-2.4596	0.0507
0.3656	1353.60	1330.58	1316.19	1312.11	1512.36	1315.95	-1.7003	-2.7640	-3.0653	11.7288	-2.7817	0.0577
0.4225	1368.30	1343.69	1328.22	1323.76	1536.28	1327.97	-1.7984	-2.9291	-3.2553	12.2762	-2.9476	0.0613
0.4952	1386.10	1360.54	1344.24	1339.43	1559.36	1343.98	-1.8440	-3.0197	-3.3669	12.4996	-3.0385	0.0632
0.5659	1402.10	1377.03	1360.57	1355.59	1573.66	1360.31	-1.7880	-2.9621	-3.3170	12.2359	-2.9804	0.0620
0.6359	1416.80	1393.46	1377.51	1372.57	1579.67	1377.26	-1.6472	-2.7733	-3.1218	11.4957	-2.7905	0.0579
0.7025	1429.80	1409.19	1394.39	1389.71	1577.87	1394.17	-1.4413	-2.4762	-2.8040	10.3562	-2.4918	0.0514
0.7812	1444.10	1427.90	1415.39	1411.32	1566.24	1415.21	-1.1218	-1.9879	-2.2699	8.4580	-2.0006	0.0410
0.8525	1456.30	1444.96	1435.48	1432.31	1546.84	1435.34	-0.7785	-1.4300	-1.6477	6.2174	-1.4393	0.0292
0.9199	1467.40	1461.19	1455.46	1453.50	1520.89	1455.38	-0.4232	-0.8135	-0.9471	3.6452	-0.8190	0.0165
1.0000	1480.60	1480.60	1480.60	1480.61	1480.60	1480.60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 6: U^2/U^2_{imix} values for all five systems studied at temperatures 303.15K and 308.15K

Ethylaniline + chloro benzene			Ethylaniline + bromo benzene			Ethylaniline + 1,2 dichloro benzene			Ethylaniline + 1,3 dichloro benzene			Ethylaniline + 1,2,4 -trichloro benzene		
X_1	303.15 K	308.15 K	X_1	303.15 K	308.15 K	X_1	303.15 K	308.15 K	X_1	303.15 K	308.15 K	X_1	303.15 K	308.15 K
0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.000	1.0000	1.0000	0.0000	1.0000	1.0000
0.0629	1.0096	1.0122	0.0714	1.0086	1.0090	0.0789	1.0181	1.0199	0.0725	1.0158	1.0133	0.0875	1.0213	1.0171
0.1159	1.0169	1.0218	0.1264	1.0142	1.0150	0.1156	1.0250	1.0277	0.1256	1.0256	1.0229	0.1559	1.0349	1.0299
0.1959	1.0266	1.0348	0.1965	1.0204	1.0212	0.1659	1.0331	1.0366	0.1956	1.0365	1.0344	0.2286	1.0467	1.0417
0.2558	1.0327	1.0431	0.2605	1.0249	1.0258	0.2569	1.0440	1.0489	0.2687	1.0448	1.0444	0.2938	1.0549	1.0507
0.3298	1.0385	1.0510	0.3365	1.0287	1.0299	0.3287	1.0497	1.0552	0.3369	1.0504	1.0514	0.3656	1.0615	1.0577
0.3968	1.0420	1.0558	0.3956	1.0306	1.0318	0.3968	1.0528	1.0586	0.4056	1.0537	1.0558	0.4225	1.0649	1.0613
0.4856	1.0441	1.0588	0.4958	1.0319	1.0332	0.4925	1.0583	1.0594	0.4856	1.0546	1.0575	0.4952	1.0526	1.0632
0.5625	1.0435	1.0579	0.5606	1.0313	1.0328	0.5421	1.0528	1.0584	0.5598	1.0529	1.0555	0.5659	1.0656	1.0620
0.6359	1.0409	1.0540	0.6429	1.0290	1.0306	0.6325	1.0488	1.0536	0.6235	1.0497	1.0515	0.6359	1.0621	1.0579
0.7025	1.0367	1.0483	0.7152	1.0256	1.0273	0.6897	1.0446	1.0488	0.6925	1.0441	1.0450	0.7025	1.0562	1.0514
0.7839	1.0295	1.0384	0.7825	1.0213	1.0230	0.7659	1.0371	1.0404	0.7759	1.0352	1.0344	0.7812	1.0462	1.0410
0.8592	1.0208	1.0268	0.8628	1.0147	1.0161	0.8425	1.0275	1.0295	0.8596	1.0237	1.0219	0.8525	1.0341	1.0292
0.9215	1.0123	1.0156	0.9205	1.0092	1.0099	0.9121	1.0166	1.0177	0.9125	1.0154	1.0136	0.9199	1.0202	1.0165
1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.000	1.0000	1.0000	1.0000	1.0000	1.0000

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^2exp/U^2_{imx} 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 five 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^2_{exp}/U^2_{imix} are observed in case of Ethylaniline+ chlorobenzene (1.0441 at 303.15K), than Ethylaniline + bromobenzene (1.0319 at 303.15K) at nearly equimolar composition at all measured temperatures due to specific interactions/complex formations between unlike molecules through hydrogen bonding. Ethylaniline + chlorobenzene systems also showed decreasing values for U^2_{exp}/U^2_{imix} , as revealed from table 6 .The U^2_{exp}/U^2_{imix} values of all five binaries have been shown in table 6

Figs 1-5 represent the variation of U^2_{exp} / U^2_{imx} with mole fraction of Ethylaniline with all five studied binary systems It is observed that in Ethylaniline+ chlorobenzene + bromobenzene systems it is maximum at approximately 0.48M and in the case of and Ethylaniline and 1, 2-dichlorobenzene + 1, 3-dichlorobenzene + 1, 2, 4-trichlorobenzene systems it is minimum at approximately 0.49 M at all the temperatures.

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. When the values of interaction parameters show positive sign, it represents strong interaction between the mixing molecules. 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 1, 2-dichlorobenzene to 1, 2, 4-trichlorobenzene .

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 temperatures. [26] On increasing the temperature, the ultrasonic velocity values decrease in the five binary liquid mixtures. This is probably due to the fact that the thermal energy activates the molecule, which would increase the rate of association of unlike molecules.

Conclusion:

The application of various ultrasonic velocity theories have been studied with binary mixtures of N-ethylaniline with chlorobenzene, bromobenzene, 1,2,dichloroethane,1,3, dichloroethane and 1,2,4 trichloroethane. 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 Nomoto Van Dael and Vangeel, and Impedance relation, in deriving the empirical relations have been truly observed in the studied binary liquid mixtures.

References:

1. G.V. Rama Rao, A.Viswanatha Sarma, J. Sivarama Krishna and C. Rambabu, Indian J Pure Appl.Phys., 2005; 43: 345
2. P .Vasantharani, S.Muthu Shailaja, A N Kannappan and R. Ezhil Pavai, J Appl. Science 2008;8(12) :2329-2332
3. S.L. Oswal, V. Pandiyan, B. Krishnakumar and P. Vasantharani, Thermochim. Acta, 2010;507: 27
4. J .D. Pandey., Ranjan Dey , D .K. Dwivedi, Pramana J Phys., 1999; .52(2): 187
5. T .Sumathi , J .Umamaheswari, Indian J Pure Appl Phys., 2009; 47:782
6. D. Bala Karuna Kumar, K. Rayapa Reddy, G. Srinivasa Rao G. V. Rama Rao , C. Rambabu , Asian Journal of Chemistry;2012;Vol. 24 Issue 5:2239
7. A .Ali, A.Yasmin , A.K.Nain, Indian J Pure Appl Phys., 2002;40: 315
8. K. Rayapa Reddy, D. Bala Karuna Kumar , C. Rambabu , G. Srinivasa Rao, E-Journal of Chemistry, 2012; 9(2): 553-562
9. Anwar Ali,Anil Kumar Nain , Soghra Hyder, J Pure Appl Ultrason., 2001; 23: 73
10. O .Nomoto, J Phys Soc, Japan, 1949;4: 280
11. W.Van Dael , E .Vangeel, Pro Int Conf on Calorimetry and Thermodynamics, Warsaw 1955;555.
12. Shipra Baluja , P.H. Parsania, Asian J Chem., 1955;7: 417.
13. R.Rao, Velocity of Sound in Liquids and Chemical Constitution, J Chem Phys,1941; 9 : 682
14. Z. Junjie, J China Univ Sci Techn, 1984;14: 298.
15. R .T. Langeman , J .E. Correy, J Chem Phys, 1942;10: 759.
16. G .R. Rendal, Proc Ind Acad Sci, 1942;16A: 369
17. D. Auslander , L. Onitni, Acustica, 1971;24:205.
18. K .Samal & S .C. Misra, J Phys Soc Japan, 1972;31: 1615.
19. R .A. Aziz, D. H .Bowman , C. Lim, Can J Phys, 1972;50: 721
20. G .R. Poole , R.A.Aziz, ibid, 1972;50:646.
21. B.A.Younglove, J Acoust Soc Am, 1965;38: 43
22. P.S.Nikam, B.S.Jagdale, A.B.Sawant , Mehdi Hasan, J Pure Appl Ultrason, 2000;22: 115.
23. A.Ali, , A.K.Nain, J Pure Appl Ultrason, 2000;22: 10.
24. A .Pal , Y. P. Singh, J Chem Eng Data., 1995; 40: 818.
25. J .A. Reddick, W. B. Bungar and T .Sakano, Organic solvents: Physical Properties and methods of purification, 4th Edn. Wiley Interscience, New York, 1986
26. Zareena Begum, P.B Sandhya Sri, C.Rambabu, ISRN Physical Chemistry, Volume 2012, Article ID 943429, doi:10.5402/2012/943429.