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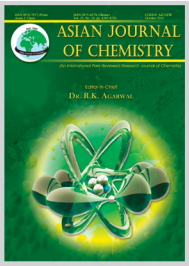

Theoretical Evaluation and Comparative Study of Ultrasonic Velocities in Binary Liquid Mixtures of N-Methyl-2-pyrrolidone with Substituted Benzenes at Different Temperatures and Atmospheric Pressure

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Theoretical velocities of binary liquid mixtures of N-methyl-2-pyrrolidone (NMP) with aniline (AB), bromobenzene (BB) and chlorobenzene (CB) at temperature = (303.15, 308.15, 313.15, 318.15) K and atmospheric pressure have been evaluated by using theoretical models such as Nomoto, Van Dael-Vangeel ideal mixing, impedance dependence, Rao's specific velocity method and Junjie's relations. Ultrasonic velocities and densities of these mixtures have also been measured experimentally as a function of composition of N-methyl-2-pyrrolidone and temperature. A good agreement is found between experimental and theoretical values. U^2_{exp}/U^2_{imx} has also been evaluated for non-ideality in the mixtures. Chi-square test for the goodness of the fit is applied to investigate the relative applicability of these theories to the present systems. The results are discussed in terms of intermolecular interactions between the component molecules in these binary liquid mixtures.

Key Words: Ultrasonic velocity, Binary mixtures, N-Methyl-2-pyrrolidone, Theoretical evaluation, Molecular interactions.

INTRODUCTION

The present work is a continuation of our research programme on thermodynamic, thermoacoustic and transport behaviour of binary liquid mixtures of industrially important components[1-4]. The study of intermolecular interaction plays an important role in the development of molecular sciences. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like infrared, Raman effect, nuclear magnetic resonance, dielectric constant, UV-visible and ultrasonic method[5]. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behaviour of liquids and solids owing to its ability of characterizing physiochemical behaviour of the medium. Rendall[6] has shown a close agreement between the experimental and theoretical values calculated from the adiabatic compressibility measurements. Several researchers[7-10] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto[11], Van Dael and Vangeel[12], Rao's specific velocity[13], impedance relation[9] and Junjie's equation[14] with reference to molecular interactions.

Compounds containing the amide group are of great concern in connection with a number of structural problems in molecular biology and constitute a simple model system for proteins. Lactams are significant class of amides not extensively studied and their solution properties are still not well understood. Hence one of the lactams, N-methyl-2-pyrrolidone (NMP) is chosen as a common solvent for the present study. It is also known that N-methyl-2-pyrrolidone interact with substituted benzenes (aromatic hydrocarbons) by dipole-dipole interactions and form some charge-transfer complexes[15,16].

In this paper we report the experimental and theoretical ultrasonic velocities of the binary liquid mixtures of N-methyl-2-pyrrolidone with chlorobenzene, bromobenzene and aniline at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range, evaluated by using various theories such as Nomoto, Van Dael and Vangeel, impedance relation, Rao's specific velocity and Junjie's relation. Further a comparative study of theoretical results with experimental values using Chi-square test and the study of molecular interactions from the deviation in the value of U^2_{exp}/U^2_{imx} (from unity) have also been reported.

EXPERIMENTAL

The commercially available pure solvents were used in the present investigation. NMP (Merck > 99 %) was distilled at low pressure and stored over freshly activated 3 Å molecular sieves. Chlorobenzene (CB), bromobenzene (BB) and aniline of AR grade procured from S.D fine chemicals (India) were purified by using fractionating column[17] and the middle fractions were used for the experimental study. The purity of the chemicals was assessed by comparing their measured densities (ρ) and ultrasonic velocities (U) which were in good agreement with literature values.

The mixtures were prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of ± 1 × 10^{-7} Kg and were stored in air-tight glass bottles. The uncertainty in mole fraction was estimated to be less than 1 × 10^{-4}. It was ensured that the components were adequately mixed before being transferred in to the apparatus. The required properties were measured within one day of the mixture preparation.

The densities (ρ) of pure liquids and their mixtures were determined using a 10^{-5} m^3 double-arm pycnometer as described by Nikam *et al.*[18]. The density values from triplicate replication at each temperature were reproducible within (4 × 10^{-2} Kg m^{-3}). The ultrasonic velocity of pure components and their mixtures were measured by single crystal variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model-F 05). The measurements of ultrasonic velocity were taken at a fixed frequency of 2 MHz. The measured speeds of sound were found to be accurate up to 0.1 m s^{-1}. Temperature control for the measurement of density and ultrasonic sound speed was achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ± 0.01 K, using a proportional temperature controller.

Theoretical considerations: On assuming the additivity of molar sound velocity (R) and no volume change on mixing, Nomoto established the following relation[11] for a liquid mixture:

$$U_{nom} = \left[\frac{(x_1R_1 + x_2R_2)}{(x_1V_1 + x_2V_2)}\right]^3 \quad (1)$$

where x_1, x_2 are the mole fractions of the species and R is related to molecular weight, density and ultrasonic velocity as $R = (M/\rho)U^{1/3} = V_mU^{1/3}$; V_m is the molar volume.

The ideal mixing theory advanced by Van Dael and VanGeel[12] in the light of assumptions made by Blandamer and Waddington[19] yield the following relation for ultrasonic velocity in liquid mixtures as

$$(x_1M_1 + x_2M_2)\times\left(\frac{1}{U_{imx}^2}\right) = \left(\frac{x_1}{M_1U_1^2} + \frac{x_2}{M_2U_2^2}\right) \quad (2)$$

where U_{imx} is the ideal mixing ultrasonic velocity in liquid mixture. U_1 and U_2 are ultrasonic velocity in species.

The sound velocity in the mixture can be predicted from the knowledge of acoustic impedance and the density of pure components. For binary mixtures, using impedance relation ultrasonic velocity is calculated by the expression[9]

$$U_{ir} = \frac{\sum x_iZ_i}{\sum x_id_i} \quad (3)$$

where x_i mole fraction, d_i is density and Z_i is the acoustic impedance.

Using Rao's specific velocity method, ultrasonic speed is calculated by using the expression[13]

$$U_{rao} = \left(\sum x_ir_id\right)^3 \quad (4)$$

where x_i mole fraction, 'd' the density of the mixture and r_i is the Rao's specific sound velocity and $r_i = U_i^{1/3}/\rho_i$.

Jungie equation[14] to calculate ultrasonic velocity is given by

$$U_j = \left[\frac{\left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right)}{\left\{(x_1M_1 + x_2M_2)^{1/2}\left(\frac{x_1M_1}{\rho_1^2U_1^2} + \frac{x_2M_2}{\rho_2^2U_2^2}\right)^{1/2}\right\}}\right] \quad (5)$$

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

According to Pearson, Chi-square test[20] for goodness of fit is given by

$$\text{Chi - suare } |\chi^2| = \sum_{i=1}^{n}\left[\frac{(O_i - E_i)^2}{E_i}\right] \quad (6)$$

where O_i (i = 1, 2, .., n) is set of observed or experimental values and E_i (i = 1, 2, .., n) is the set of expected or theoretical values. Interaction parameter (α) is calculated by using the expression, $a = U^2_{exp}/U^2_{imx} - 1$.

RESULTS AND DISCUSSION

The experimental and theoretical velocities calculated by using the eqns. 1-5 are presented in Tables 1-3 for all the three binary systems at temperatures 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure. The validity of different theoretical formulae is checked by the Chi-square test for all the mixtures at all the temperatures and the values are given in Table-4. It can be seen from Tables 1-4 that the theoretical values of ultrasonic velocity computed by various theories show deviations from experimental values. The limitations and approximations incorporated in these theories are responsible for the deviations of theoretical velocities from experimental values. In Nomoto's theory, no interaction between the components of liquid mixtures has been taken into account as it is supposed that the volume does not change on mixing. Similarly, the assumption for the formation of ideal mixing relation is that, the ratios of specific heats of ideal mixtures and the volumes are equal by not taking into the consideration of molecular interactions. Various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions are operative due to interactions when two liquids are mixed. Thus, the observed deviation of theoretical values of velocity from the experimental

TABLE-1
EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM N-METHYL-2-PYRROLIDONE + ANILINE

x	U_{ir}	U_j	U_{rao}	U_{nom}	U_{imx}	U_{expt}	U_{ir} (%)	U_{rao} (%)	U_j (%)	U_{nom} (%)	U_{imx} (%)	α
						303.15 K						
0.0000	1617.6	1617.6	1617.6	1617.6	1617.6	1617.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0954	1611.4	1610.8	1626.1	1611.0	1611.2	1615.4	-0.25	0.66	-0.28	-0.27	-0.26	0.0053
0.1918	1605.1	1604.1	1631.3	1604.5	1604.7	1613.3	-0.51	1.12	-0.57	-0.55	-0.53	0.0108
0.2892	1598.7	1597.4	1635.2	1598.0	1598.2	1611.5	-0.79	1.47	-0.87	-0.84	-0.82	0.0167
0.3876	1592.3	1590.9	1633.7	1591.5	1591.8	1608.0	-0.97	1.60	-1.07	-1.03	-1.01	0.0205
0.4870	1585.9	1584.4	1629.2	1585.0	1585.3	1604.1	-1.14	1.56	-1.23	-1.19	-1.17	0.0239
0.5875	1579.4	1577.9	1622.2	1578.5	1578.8	1596.7	-1.09	1.59	-1.18	-1.14	-1.12	0.0228
0.6890	1572.8	1571.5	1608.9	1572.1	1572.3	1588.0	-0.96	1.31	-1.04	-1.00	-0.99	0.0201
0.7915	1566.2	1565.2	1593.7	1565.6	1565.8	1577.0	-0.69	1.06	-0.75	-0.72	-0.71	0.0143
0.8952	1559.5	1559.0	1576.2	1559.2	1559.3	1565.0	-0.35	0.72	-0.38	-0.37	-0.36	0.0073
1.0000	1552.8	1552.8	1552.8	1552.8	1552.8	1552.8	0.00	0.00	0.00	0.00	0.00	0.0000
						308.15 K						
0.0000	1595.8	1595.8	1595.8	1595.8	1595.8	1595.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.0954	1589.1	1588.5	1605.6	1588.8	1588.9	1593.4	-0.27	0.77	-0.31	-0.29	-0.28	0.0057
0.1918	1582.4	1581.3	1610.9	1581.8	1582.0	1590.4	-0.50	1.29	-0.57	-0.54	-0.53	0.0107
0.2892	1575.6	1574.1	1613.2	1574.8	1575.0	1588.1	-0.79	1.58	-0.88	-0.84	-0.82	0.0167
0.3876	1568.7	1567.1	1611.3	1567.8	1568.1	1584.9	-1.02	1.67	-1.12	-1.08	-1.06	0.0215
0.4870	1561.8	1560.1	1607.3	1560.9	1561.2	1580.8	-1.20	1.68	-1.31	-1.26	-1.24	0.0253
0.5875	1554.8	1553.2	1599.8	1553.9	1554.2	1572.8	-1.14	1.72	-1.24	-1.20	-1.18	0.0240
0.6890	1547.8	1546.4	1586.7	1547.0	1547.3	1563.5	-1.00	1.49	-1.09	-1.05	-1.04	0.0211
0.7915	1540.7	1539.7	1570.6	1540.1	1540.3	1552.0	-0.73	1.20	-0.79	-0.77	-0.75	0.0152
0.8952	1533.6	1533.0	1551.7	1533.3	1533.4	1540.0	-0.42	0.76	-0.45	-0.44	-0.43	0.0087
1.0000	1526.4	1526.4	1526.4	1526.4	1526.4	1526.4	0.00	0.00	0.00	0.00	0.00	0.0000
						313.15 K						
0.0000	1577.6	1577.6	1577.6	1577.6	1577.6	1577.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0954	1570.2	1569.5	1589.5	1569.8	1569.9	1574.7	-0.28	0.94	-0.33	-0.31	-0.30	0.0061
0.1918	1562.8	1561.5	1593.7	1562.1	1562.3	1572.0	-0.59	1.38	-0.67	-0.63	-0.62	0.0125
0.2892	1555.3	1553.5	1593.2	1554.3	1554.6	1568.8	-0.86	1.55	-0.97	-0.92	-0.90	0.0183
0.3876	1547.7	1545.7	1592.1	1546.6	1547.0	1566.0	-1.17	1.66	-1.29	-1.24	-1.22	0.0248
0.4870	1540.1	1538.0	1586.4	1539.0	1539.3	1562.1	-1.41	1.56	-1.54	-1.48	-1.46	0.0298
0.5875	1532.4	1530.4	1577.4	1531.3	1531.7	1553.0	-1.33	1.57	-1.45	-1.40	-1.37	0.0281
0.6890	1524.7	1522.9	1564.4	1523.7	1524.0	1541.4	-1.09	1.49	-1.20	-1.15	-1.13	0.0230
0.7915	1516.8	1515.5	1547.7	1516.1	1516.3	1528.1	-0.74	1.29	-0.82	-0.78	-0.77	0.0156
0.8952	1509.0	1508.2	1526.9	1508.5	1508.7	1515.0	-0.40	0.79	-0.45	-0.43	-0.42	0.0084
1.0000	1501.0	1501.0	1501.0	1501.0	1501.0	1501.0	0.00	0.00	0.00	0.00	0.00	0.0000
						318.15 K						
0.0000	1556.0	1556.0	1556.0	1556.0	1556.0	1556.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0954	1548.5	1547.7	1569.4	1548.1	1548.2	1553.9	-0.35	0.99	-0.40	-0.37	-0.37	0.0074
0.1918	1540.9	1539.5	1574.0	1540.2	1540.4	1552.1	-0.72	1.41	-0.81	-0.77	-0.75	0.0153
0.2892	1533.3	1531.5	1574.0	1532.3	1532.6	1549.5	-1.05	1.58	-1.16	-1.11	-1.09	0.0222
0.3876	1525.6	1523.5	1571.6	1524.5	1524.8	1546.0	-1.32	1.66	-1.46	-1.39	-1.37	0.0280
0.4870	1517.8	1515.7	1564.8	1516.7	1517.0	1541.0	-1.50	1.54	-1.64	-1.58	-1.56	0.0319
0.5875	1510.0	1507.9	1555.6	1508.9	1509.2	1532.1	-1.44	1.53	-1.58	-1.52	-1.50	0.0306
0.6890	1502.1	1500.3	1542.5	1501.1	1501.4	1519.0	-1.11	1.55	-1.23	-1.18	-1.16	0.0236
0.7915	1494.1	1492.8	1526.3	1493.4	1493.6	1506.2	-0.80	1.34	-0.89	-0.85	-0.84	0.0170
0.8952	1486.1	1485.3	1505.0	1485.7	1485.8	1492.5	-0.43	0.84	-0.48	-0.46	-0.45	0.0090
1.0000	1478.0	1478.0	1478.0	1478.0	1478.0	1478.0	0.00	0.00	0.00	0.00	0.00	0.0000

values shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture.

It is observed from Tables 1 and 4, for N-methyl-2-pyrrolidone + aniline system, that there is a close agreement in impedance and Van Deal VanGeel velocities with experimental velocities, slight deviation in Nomoto's relation from experimental values whereas higher deviations are observed in Rao's relation. There is a good agreement between experimental and theoretical values in Nomoto relation, slight deviations are observed in Van Deal VanGeel and impedance relation method whereas higher deviations are observed in Rao's specific velocity at all the temperatures for N-methyl-2-pyrrolidone + bromobenzene or N-methyl-2-pyrrolidone + chlorobenzene systems over the miscibility region $0 < x < 1$ (Tables 2-4).

Fig. 1 indicates the deviation of the ratio U^2_{exp}/U^2_{imx} as a function of mole fraction of N-methyl-2-pyrrolidone at different temperatures for all the three binary mixtures. The deviation of the ratio U^2_{exp}/U^2_{imx} from unity (interaction parameter, α) is a direct measure of non-ideality of the binary liquid mixture as a consequence of association or charge transfer *etc*. The positive values of 'α' in all the three systems at all the four

TABLE-2
EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM N-METHYL-2-PYRROLIDONE + BROMOBENZENE

x	U_{ir}	U_j	U_{rao}	U_{nom}	U_{imx}	U_{expt}	U_{ir} (%)	U_{rao} (%)	U_j (%)	U_{nom} (%)	U_{imx} (%)	α
						303.15 K						
0.0000	1138.0	1138.0	1138.0	1138.0	1138.0	1138.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1084	1170.2	1169.1	1245.8	1175.7	1171.0	1173.0	-0.24	6.20	-0.33	0.23	-0.17	0.0035
0.2149	1204.0	1202.0	1357.6	1214.2	1205.4	1210.2	-0.51	12.18	-0.68	0.33	-0.39	0.0079
0.3193	1239.6	1236.8	1441.9	1253.5	1241.5	1248.0	-0.68	15.53	-0.90	0.44	-0.52	0.0105
0.4219	1277.1	1273.7	1521.6	1293.7	1279.3	1287.1	-0.78	18.22	-1.04	0.51	-0.61	0.0122
0.5226	1316.6	1312.9	1575.0	1334.7	1319.0	1328.0	-0.86	18.60	-1.14	0.50	-0.68	0.0137
0.6215	1358.5	1354.6	1606.9	1376.6	1360.8	1369.3	-0.79	17.35	-1.07	0.53	-0.62	0.0126
0.7186	1402.8	1399.2	1625.6	1419.3	1404.8	1412.6	-0.69	15.08	-0.95	0.47	-0.55	0.0111
0.8141	1449.8	1446.8	1617.6	1462.9	1451.3	1457.0	-0.50	11.02	-0.70	0.41	-0.39	0.0078
0.9078	1499.7	1497.9	1596.3	1507.4	1500.6	1504.2	-0.30	6.12	-0.42	0.21	-0.24	0.0049
1.0000	1552.8	1552.8	1552.8	1552.8	1552.8	1552.8	0.00	0.00	0.00	0.00	0.00	0.0000
						308.15 K						
0.0000	1123.0	1123.0	1123.0	1123.0	1123.0	1123.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1084	1154.3	1153.3	1237.1	1159.7	1155.1	1157.9	-0.31	6.84	-0.39	0.15	-0.24	0.0048
0.2149	1187.1	1185.4	1341.5	1197.2	1188.7	1194.0	-0.57	12.35	-0.72	0.27	-0.45	0.0090
0.3193	1221.8	1219.3	1434.0	1235.4	1223.8	1231.0	-0.75	16.49	-0.95	0.36	-0.59	0.0119
0.4219	1258.2	1255.2	1508.0	1274.5	1260.6	1269.5	-0.89	18.79	-1.13	0.40	-0.70	0.0142
0.5226	1296.7	1293.4	1557.1	1314.4	1299.2	1309.0	-0.94	18.95	-1.19	0.41	-0.75	0.0152
0.6215	1337.4	1334.0	1589.7	1355.1	1339.8	1350.0	-0.93	17.76	-1.19	0.38	-0.75	0.0153
0.7186	1380.5	1377.3	1610.5	1396.7	1382.6	1391.7	-0.81	15.72	-1.04	0.36	-0.65	0.0132
0.8141	1426.2	1423.6	1598.6	1439.1	1427.8	1436.0	-0.68	11.32	-0.87	0.21	-0.57	0.0115
0.9078	1474.7	1473.1	1584.8	1482.3	1475.6	1481.3	-0.44	6.99	-0.55	0.07	-0.38	0.0077
1.0000	1526.4	1526.4	1526.4	1526.4	1526.4	1526.4	0.00	0.00	0.00	0.00	0.00	0.0000
						313.15 K						
0.0000	1110.0	1110.0	1110.0	1110.0	1110.0	1110.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1084	1140.3	1139.5	1221.5	1145.6	1141.2	1144.3	-0.35	6.75	-0.42	0.11	-0.27	0.0055
0.2149	1172.2	1170.6	1322.0	1181.9	1173.8	1180.0	-0.66	12.03	-0.80	0.16	-0.53	0.0107
0.3193	1205.8	1203.5	1411.4	1219.0	1207.8	1216.0	-0.84	16.07	-1.02	0.25	-0.67	0.0136
0.4219	1241.2	1238.4	1486.9	1256.9	1243.5	1253.8	-1.01	18.59	-1.23	0.25	-0.82	0.0166
0.5226	1278.5	1275.4	1537.2	1295.6	1281.0	1292.0	-1.05	18.98	-1.28	0.28	-0.86	0.0173
0.6215	1317.9	1314.8	1566.0	1335.1	1320.3	1331.4	-1.01	17.62	-1.25	0.27	-0.83	0.0169
0.7186	1359.7	1356.8	1583.5	1375.3	1361.8	1372.5	-0.93	15.37	-1.15	0.21	-0.78	0.0158
0.8141	1403.9	1401.6	1567.5	1416.4	1405.6	1415.3	-0.80	10.76	-0.97	0.08	-0.69	0.0139
0.9078	1451.0	1449.5	1545.4	1458.3	1451.9	1458.0	-0.48	5.99	-0.58	0.02	-0.42	0.0085
1.0000	1501.0	1501.0	1501.0	1501.0	1501.0	1501.0	0.00	0.00	0.00	0.00	0.00	0.0000
						318.15 K						
0.0000	1096.0	1096.0	1096.0	1096.0	1096.0	1096.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1084	1125.6	1124.9	1202.6	1130.9	1126.5	1130.4	-0.43	6.39	-0.48	0.04	-0.35	0.0069
0.2149	1156.6	1155.4	1302.4	1166.5	1158.3	1165.0	-0.72	11.79	-0.82	0.13	-0.57	0.0115
0.3193	1189.4	1187.7	1395.7	1202.8	1191.6	1200.3	-0.91	16.28	-1.05	0.21	-0.72	0.0146
0.4219	1223.9	1221.8	1465.5	1239.9	1226.5	1237.0	-1.06	18.47	-1.23	0.23	-0.85	0.0172
0.5226	1260.3	1258.0	1512.9	1277.7	1263.1	1275.0	-1.15	18.66	-1.33	0.21	-0.93	0.0189
0.6215	1298.9	1296.5	1541.6	1316.2	1301.6	1314.1	-1.16	17.31	-1.34	0.16	-0.95	0.0194
0.7186	1339.7	1337.5	1543.2	1355.5	1342.1	1354.0	-1.06	13.97	-1.22	0.11	-0.88	0.0179
0.8141	1383.0	1381.1	1548.8	1395.6	1384.8	1395.5	-0.90	10.98	-1.03	0.01	-0.77	0.0155
0.9078	1429.0	1427.9	1528.6	1436.4	1430.0	1437.4	-0.59	6.35	-0.66	-0.07	-0.51	0.0103
1.0000	1478.0	1478.0	1478.0	1478.0	1478.0	1478.0	0.00	0.00	0.00	0.00	0.00	0.0000

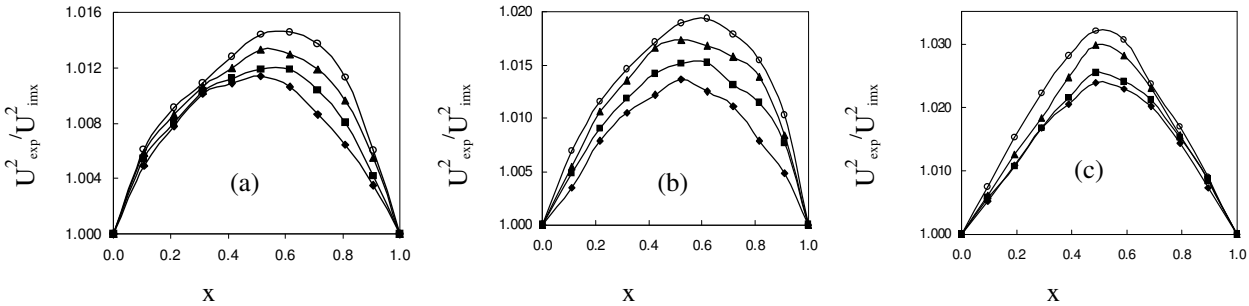

Fig. 1. Variation of U^2_{exp}/U^2_{imx}, against mole fraction of N-methyl-2-pyrrolidone(x) for the system N-methyl-2-pyrrolidone + chlorobenzene (a), N-methyl-2-pyrrolidone + bromobenzene (b) N-methyl-2-pyrrolidone + aniline (c) at temperatures 303.15 K, ♦, 308.15 K, ■, 313.15 K, ▲, 318.15 K ○

TABLE-3
EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM N-METHYL-2-PYRROLIDONE + CHLOROBENZENE

x	U_{ir}	U_j	U_{rao}	U_{nom}	U_{imx}	U_{expt}	U_{ir} (%)	U_{rao} (%)	U_j (%)	U_{nom} (%)	U_{imx} (%)	α
						303.15 K						
0.0000	1250.0	1250.0	1250.0	1250.0	1250.0	1250.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1055	1280.1	1273.8	1290.7	1278.3	1275.8	1279.5	0.08	0.91	-0.41	-0.05	-0.25	0.0050
0.2097	1310.2	1298.7	1330.4	1307.1	1302.5	1309.3	0.20	1.74	-0.68	-0.04	-0.39	0.0078
0.3127	1340.3	1324.8	1368.1	1336.3	1330.1	1339.0	0.26	2.34	-0.89	-0.04	-0.50	0.0101
0.4144	1370.5	1352.3	1404.6	1365.9	1358.6	1369.2	0.33	2.83	-1.00	-0.01	-0.54	0.0109
0.5149	1400.8	1381.2	1437.6	1395.9	1388.1	1400.0	0.34	2.98	-1.06	-0.01	-0.56	0.0114
0.6142	1431.1	1411.7	1466.6	1426.4	1418.7	1429.0	0.34	2.83	-1.02	0.01	-0.53	0.0106
0.7124	1461.5	1443.9	1494.9	1457.3	1450.3	1458.5	0.33	2.63	-0.87	0.05	-0.43	0.0086
0.8094	1491.9	1478.1	1517.6	1488.7	1483.2	1489.2	0.26	1.99	-0.67	0.05	-0.32	0.0065
0.9052	1522.3	1514.3	1537.1	1520.5	1517.3	1521.0	0.15	1.13	-0.38	0.03	-0.18	0.0035
1.0000	1552.8	1552.8	1552.8	1552.8	1552.8	1552.8	0.00	0.00	0.00	0.00	0.00	0.0000
						308.15 K						
0.0000	1231.0	1231.0	1231.0	1231.0	1231.0	1231.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1055	1260.4	1254.1	1271.3	1258.6	1256.3	1259.7	0.06	0.92	-0.44	-0.09	-0.27	0.0055
0.2097	1289.9	1278.4	1310.2	1286.6	1282.4	1287.5	0.18	1.76	-0.71	-0.07	-0.40	0.0080
0.3127	1319.4	1303.8	1347.4	1315.0	1309.3	1316.0	0.25	2.39	-0.92	-0.08	-0.51	0.0103
0.4144	1348.9	1330.6	1382.6	1343.9	1337.1	1344.6	0.32	2.83	-1.04	-0.06	-0.56	0.0112
0.5149	1378.4	1358.8	1415.0	1373.2	1365.9	1374.0	0.32	2.98	-1.11	-0.06	-0.59	0.0119
0.6142	1407.9	1388.5	1443.5	1402.9	1395.7	1404.0	0.28	2.81	-1.10	-0.08	-0.59	0.0119
0.7124	1437.5	1420.0	1470.0	1433.1	1426.6	1434.0	0.24	2.51	-0.98	-0.06	-0.51	0.0104
0.8094	1467.1	1453.3	1493.5	1463.7	1458.6	1464.5	0.18	1.98	-0.76	-0.05	-0.40	0.0080
0.9052	1496.7	1488.7	1512.1	1494.8	1491.9	1495.0	0.12	1.14	-0.42	-0.01	-0.21	0.0042
1.0000	1526.4	1526.4	1526.4	1526.4	1526.4	1526.4	0.00	0.00	0.00	0.00	0.00	0.0000
						313.15 K						
0.0000	1213.0	1213.0	1213.0	1213.0	1213.0	1213.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1055	1241.7	1235.6	1253.3	1239.9	1237.7	1241.3	0.03	0.96	-0.46	-0.11	-0.29	0.0058
0.2097	1270.4	1259.3	1291.0	1267.2	1263.2	1268.6	0.14	1.76	-0.73	-0.11	-0.43	0.0086
0.3127	1299.1	1284.2	1327.9	1294.9	1289.5	1296.3	0.22	2.44	-0.94	-0.11	-0.53	0.0106
0.4144	1327.9	1310.3	1362.2	1323.1	1316.7	1324.5	0.26	2.85	-1.07	-0.11	-0.59	0.0120
0.5149	1356.7	1337.8	1393.9	1351.6	1344.7	1353.7	0.22	2.97	-1.17	-0.15	-0.66	0.0133
0.6142	1385.5	1366.8	1421.9	1380.6	1373.8	1382.7	0.20	2.83	-1.15	-0.15	-0.64	0.0130
0.7124	1414.3	1397.5	1447.6	1410.1	1403.9	1412.2	0.15	2.51	-1.04	-0.15	-0.59	0.0119
0.8094	1443.2	1429.9	1470.5	1439.9	1435.1	1442.0	0.08	1.98	-0.84	-0.14	-0.48	0.0097
0.9052	1472.1	1464.3	1488.4	1470.3	1467.4	1471.5	0.04	1.15	-0.49	-0.08	-0.28	0.0056
1.0000	1501.0	1501.0	1501.0	1501.0	1501.0	1501.0	0.00	0.00	0.00	0.00	0.00	0.0000
						318.15 K						
0.0000	1195.0	1195.0	1195.0	1195.0	1195.0	1195.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1055	1223.3	1217.1	1235.5	1221.3	1219.3	1223.0	0.02	1.02	-0.48	-0.14	-0.30	0.0061
0.2097	1251.6	1240.3	1272.9	1248.1	1244.3	1250.0	0.13	1.84	-0.78	-0.15	-0.45	0.0091
0.3127	1279.9	1264.6	1309.1	1275.3	1270.2	1277.1	0.22	2.51	-0.98	-0.14	-0.54	0.0109
0.4144	1308.2	1290.2	1343.5	1302.9	1296.9	1305.2	0.23	2.94	-1.15	-0.18	-0.64	0.0129
0.5149	1336.5	1317.2	1374.6	1331.0	1324.5	1334.0	0.19	3.04	-1.26	-0.23	-0.71	0.0144
0.6142	1364.8	1345.7	1402.2	1359.5	1353.1	1362.9	0.14	2.89	-1.26	-0.25	-0.72	0.0146
0.7124	1393.1	1375.8	1427.0	1388.4	1382.6	1392.1	0.07	2.51	-1.17	-0.26	-0.68	0.0138
0.8094	1421.4	1407.8	1448.8	1417.8	1413.3	1421.2	0.01	1.94	-0.94	-0.24	-0.56	0.0113
0.9052	1449.7	1441.8	1466.9	1447.7	1445.0	1449.4	0.02	1.21	-0.53	-0.12	-0.30	0.0061
1.0000	1478.0	1478.0	1478.0	1478.0	1478.0	1478.0	0.00	0.00	0.00	0.00	0.00	0.0000

temperatures (Tables 1-3) under study reveals the existence of strong interactions between the unlike molecules in the binary liquid mixtures under investigation. The N-methyl-2-pyrrolidone + aniline system shows maximum 'α' value, where as N-methyl-2-pyrrolidone + X (X = bromobenzene or chlorobenzene), show lesser α values. This may be due to i) the possibility of specific interactions between N-methyl-2-pyrrolidone and aniline, besides dipole-dipole interactions, due to hydrogen bond formation[21] between the CO group of N-methyl-2-pyrrolidone (which acts as hydrogen bond acceptor) and N-H of aniline which is a hydrogen bond donor ii) higher electro negative difference between the C and N of sp^2C-NH_2 bond in aniline. The replacement of -NH_2 group by chloro-group or a bromo-group in aniline resulted in lesser α values, the decreased electro negativity and the increased molecular size[22] (molecular radius of chlorobenzene is 2.16 Å, while it is 2.19 Å for bromobenzene at 298.15 K) are responsible in decreasing the strength of interaction in the binary liquid mixtures N-methyl-2-pyrrolidone + bromobenzene or N-methyl-2-pyrrolidone + chlorobenzene.

It may be concluded that out of five theories and relations, the Nomoto's relation and impedance relation provides the

TABLE-4
VALUES OF CHI-SQUARE AND SIGMA RELATIVE DEVIATION FOR ALL THE BINARY MIXTURES OF N-METHYL-2-PYRROLIDONE AT DIFFERENT TEMPERATURES

T (K)	χ^2					SdU				
	NOM[11]	IMP	VDV	JUN[12]	RAO	NOM	IMP	VDV	JUN	RAO
System I (N-methyl-2-pyrrolidone + aniline)										
303.15	1.04	0.94	1.01	1.12	2.37	-0.072	-0.068	-0.070	-0.074	0.110
308.15	1.13	1.01	1.09	1.22	2.76	-0.075	-0.071	-0.074	-0.079	0.120
313.15	1.42	1.27	1.37	1.55	2.70	-0.084	-0.079	-0.083	-0.088	0.121
318.15	1.69	1.52	1.64	1.85	2.74	-0.093	-0.088	-0.092	-0.098	0.123
System I (N-methyl-2-pyrrolidone + bromobenzene)										
303.15	0.21	0.47	0.29	0.87	271.69	0.036	-0.054	-0.042	-0.073	1.115
308.15	0.11	0.63	0.41	1.04	262.98	0.026	-0.063	-0.051	-0.081	1.105
313.15	0.05	0.80	0.54	1.19	255.82	0.016	-0.072	-0.059	-0.088	1.099
318.15	0.02	0.94	0.66	1.33	253.09	0.009	-0.079	-0.066	-0.094	1.100
System I (N-methyl-2-pyrrolidone + chlorobenzene)										
303.15	0.002	0.09	0.23	0.83	6.50	0.00001	0.023	-0.037	-0.070	0.189
308.15	0.01	0.07	0.27	0.94	6.34	-0.006	0.019	-0.041	-0.076	0.189
313.15	0.02	0.03	0.33	1.02	6.31	-0.011	0.013	-0.045	-0.080	0.190
318.15	0.05	0.02	0.39	1.18	6.47	-0.017	0.010	-0.049	-0.086	0.194

best results. Thus, the linearity of molar sound speed and additivity of molar volumes, as suggested by Nomoto[11] in deriving the empirical relation given in eqn. 1 have been truly observed in the binary liquid mixtures of N-methyl-2-pyrrolidone and bromobenzene or chlorobenzene. The success of Nomoto's relation in predicting the experimental ultrasonic speeds for polar-polar liquid mixtures has also been emphasized by others[23-25].

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