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Theoretical Evaluation of Speeds of Sound in Liquid Mixtures Containing Diethyl carbonate and Aniline at Various Temperatures

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Abstract

Speeds of sound and density values of the liquid mixtures containing diethyl carbonate and aniline have been measured at different temperatures (293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K over the entire range of mole fraction. The theoretical values of speeds of sound were evaluated with the help of Nomoto's relation (u_{NR}), impedance relation (u_{IR}), ideal mixing relation (u_{IMR}), Junjie's relaiton (u_{JR}) and Rao's specific velocity relation (u_R). The theoretical values are compared with the experimental values. The molecular association (α) has been evaluated from the values of experimental and theoretical speeds.

Keywords: Diethyl carbonate, aniline, mixing rules.

Introduction

In determining the Physico-chemical behaviour of liquid mixtures, speeds of sound data is very important and it have many applications in industry. Speeds of sound investigations has been carrying by many researchers[1-4] from several years and correlating the experimental results with the theoretical relations of Nomoto[5], impedance[6], ideal mixing relation[7], Junjie[8] and Rao's specific velocity[9]. Due to its non-destructive nature, speeds of sound of liquid mixtures have been extensively carrying out in the last two decades in different branches of science. These measurements are helpful in measuring thermodynamic properties which in turn are useful to predict the nature of molecular interactions present between molecules in a mixture.

Here we report the experimental values of speeds of sound along with theoretical values evaluated using ideal mixing relation, Nomoto's relation, Junjie's relation, impedance relation and Rao's specific velocity relation for diethyl carbonate and aniline at temperatures (293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K over the entire mole fraciton range. Relative applicability of these theories to the system considered in the present study has been checked including the necessary discussion.

Material and Methods

The present investigation used the chemicals obtained from Aldrich Chemicals with purity >99% and they were used as-received without any further purification. Purity of the samples was checked by comparison of the observed values of densities and speeds of sound with those in literature reports.

Anton Paar DSA 5000 density and sound analyser provided with two Pt 100 platinum thermometer was used for measuring densities and speeds of sound of pure liquids as well as liquid mixtures. The apparatus was controlled to ±0.001 K by a built-in solid state thermostat since density shows extreme sensitivity to temperature. The stated accuracy in speed of sound and density are 0.5 m/s and $5x10^{-3}$ kgm^{-3} respectively.

Known masses of pure liquids were mixed in order to get the binary liquid mixtures and they were stored in airtight-stoppered bottles to minimize evaporation losses. The weighings were done using an electronic balance with a precision of ±0.01mg.

Theory: Nomoto's relation, According to Nomoto, following is the relation for speed of sound in binary liquid mixtures, which was established based on the assumption of the additivity of molar sound speed (R) and no change in volume on mixing:

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

where u and ρ are determined experimentally, and M is the mean molecular weight in a binary mixture.

$$M = (x_1M_1 + x_2M_2) \quad (2)$$

Here M_1, M_2, x_1 and x_2 are molecular weights and mole fractions of constituent components.

$$u_{NR} = [(x_1R_1 + x_2R_2)/(x_1V_1+x_2V_2)]^3 \quad (3)$$

In the above equation, V_1 and V_2 are the molar volumes of 1st and 2nd components of the liquid mixture.

Impedance relaiton

$$u_{IR} = \Sigma x_i Z_i / \Sigma x_i \rho_i \quad (4)$$

where x_i is the mole fraction, ρ_i the density and Z_i is the acoustic impedance of the mixture.

Junjie equation

$$u_J = (x_1M_1/\rho_1 + x_2M_2/\rho_2)/[\{x_1M_1 + x_2M_2\}^{1/2} \{x_1M_1/\rho_1u_1^2 + x_2M_2/\rho_2u_2^2\}^{1/2}] \quad (5)$$

Rao's specific velocity

$$u_R = (\Sigma x_i r_i \rho_i)^3 \quad (6)$$

where x_i = mole fraction, ρ_i = density and r_i = Rao's specific sound velocity of the mixture.

Ideal Mixing relation

$$1/(x_1M_1 + x_2M_2)*u^2_{imx} = x_1/M_1u_1^2 + x_2/M_2u_2^2 \quad (7)$$

The degree of molecular interaction given as interaction parameter, α is calculated using the relation,

$$\alpha = (u_{exp}^2/u_{imx}^2) - 1 \quad (8)$$

Results and Discussion

The experimentally obtained values of speeds of sound for the binary system and the corresponding theoretical values at various temperatures are presented in table-1. Data reveals that the speeds of sound calculated from Ideal Mixing relation (IMR) exhibit more satisfactory agreement with the experimental values in all the temperatures studied than other approaches in the binary system. From table-2 it is observed that there is a deviation between experimental and theoretical values which confirms the existence of molecular interactions. Higher variations are observed at some intermediate concentrations suggesting the strong tendency of association between component molecules of the mixture due to hydrogen bonding[10]. Interactions between different components of the binary mixture were not taken into account in view of the assumption in Nomoto's theory, that there is no change in the volume on mixing. In case of ideal mixing relation, the ratios of specific heats of ideal mixtures and the volumes are also equal and hence no molecular interactions are considered. However, upon mixing the components, interactions between the molecules occur due to the presence of various types of forces like hydrogen bonding, charge transfer, dispersion forces and interactions of dipole-dipole and dipole-induced dipole. The deviations observed in case of theoretical values of speeds of sound from the experimental values, thus, indicate that there are molecular interactions between the unlike molecules[11].

The negative and positive magnitudes of percentage deviations in speeds of sound indicating non ideal behavior of liquid mixtures. The positive value of α at all temperatures clearly indicates the existence of strong tendency for the formation of association in mixture through dipole-dipole interactions. All the theoretical models fairly predicted the speeds of sound are reasonably close to the experimental values.

Conclusion

Speeds of sound values are measured at different temperatures and using various theoretical models speeds of sound is evaluated. Experimental values are compared with the theoretical results and it is observed that Ideal Mixing relation provides good results when compared to other relations.

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Table-1
Experimental and theoretical values of speeds of sound for diethyl carbonate + aniline at different temperatures

x_1	u_{expt}	u_{NR}	u_{IR}	u_{IMR}	u_{JR}	u_R	u_{expt}	u_{NR}	u_{IR}	u_{IMR}	u_{JR}	u_R
	293.15 K						298.15 K					
0.0000	1656.02	1656.02	1656.02	1656.02	1656.02	1656.02	1636.79	1636.79	1636.79	1636.79	1636.79	1636.79
0.0730	1613.70	1608.31	1624.00	1610.52	1585.99	1621.09	1594.43	1588.81	1604.72	1590.86	1565.85	1601.75
0.1652	1562.65	1552.43	1583.28	1556.69	1513.50	1576.35	1543.34	1532.64	1563.93	1536.62	1492.70	1556.87
0.2537	1516.89	1502.81	1543.82	1508.37	1456.18	1534.35	1497.74	1482.80	1524.40	1488.01	1435.05	1514.72
0.3387	1475.49	1458.60	1505.67	1464.87	1409.74	1494.76	1455.94	1438.42	1486.17	1444.31	1388.48	1475.01
0.4432	1427.55	1408.25	1458.32	1414.79	1361.40	1447.05	1407.88	1387.92	1438.69	1394.07	1340.11	1427.15
0.5468	1381.13	1362.29	1410.90	1368.50	1320.87	1399.34	1361.32	1341.85	1391.13	1347.70	1299.65	1379.30
0.6546	1335.93	1318.20	1361.08	1323.56	1284.82	1350.64	1315.96	1297.69	1341.16	1302.75	1263.72	1330.37
0.7559	1294.35	1279.86	1313.82	1284.02	1255.44	1305.27	1274.23	1259.32	1293.73	1263.24	1234.49	1284.98
0.8840	1242.96	1235.18	1253.36	1237.34	1223.26	1249.50	1222.58	1214.61	1233.04	1216.66	1202.51	1229.05
1.0000	1198.01	1198.01	1198.01	1198.01	1198.01	1198.01	1177.46	1177.46	1177.46	1177.46	1177.46	1177.46
	303.15 K						308.15 K					
0.0000	1617.52	1617.52	1617.52	1617.52	1617.52	1617.52	1598.27	1598.27	1598.27	1598.27	1598.27	1598.27
0.0730	1575.11	1569.26	1585.41	1571.16	1545.66	1582.36	1555.8	1549.75	1566.13	1551.49	1525.49	1563.00
0.1652	1523.92	1512.81	1544.56	1516.51	1471.85	1537.34	1504.55	1493.04	1525.24	1496.44	1451.04	1517.87
0.2537	1478.31	1462.77	1504.96	1467.62	1413.89	1495.08	1458.49	1442.79	1485.58	1447.27	1392.79	1475.46
0.3387	1436.36	1418.23	1466.65	1423.72	1367.20	1455.24	1416.83	1398.11	1447.21	1403.20	1345.99	1435.54
0.4432	1388.18	1367.59	1419.06	1373.33	1318.81	1407.23	1368.52	1347.34	1399.52	1352.67	1297.61	1387.41
0.5468	1341.47	1321.42	1371.38	1326.90	1278.43	1359.27	1321.69	1301.09	1351.73	1306.19	1257.32	1339.33
0.6546	1295.96	1277.20	1321.27	1281.94	1242.63	1310.33	1276.04	1256.82	1301.48	1261.25	1221.68	1290.28
0.7559	1254.09	1238.80	1273.68	1242.49	1213.56	1264.74	1234.06	1218.41	1253.76	1221.86	1192.78	1244.61
0.8840	1202.27	1194.09	1212.77	1196.02	1181.81	1208.67	1182.09	1173.71	1192.64	1175.52	1161.25	1188.43
1.0000	1156.96	1156.96	1156.96	1156.96	1156.96	1156.96	1136.62	1136.62	1136.62	1136.62	1136.62	1136.62
	313.15 K						318.15 K					
0.0000	1579.10	1579.10	1579.10	1579.10	1579.10	1579.10	1559.95	1559.95	1559.95	1559.95	1559.95	1559.95
0.0730	1536.56	1530.33	1546.94	1531.90	1505.39	1543.73	1517.56	1510.93	1527.79	1512.34	1485.33	1524.50
0.1652	1485.25	1473.36	1506.01	1476.44	1430.31	1498.47	1466.00	1453.73	1486.83	1456.50	1409.63	1479.13
0.2537	1439.08	1422.92	1466.31	1427.01	1371.78	1455.94	1419.76	1403.12	1447.10	1406.81	1350.85	1436.50
0.3387	1397.37	1378.11	1427.87	1382.77	1324.88	1415.93	1377.98	1358.19	1408.62	1362.42	1303.87	1396.41
0.4432	1348.95	1327.22	1380.11	1332.13	1276.52	1367.69	1329.49	1307.20	1360.79	1311.68	1255.56	1348.07
0.5468	1302.02	1280.90	1332.22	1285.61	1236.35	1319.51	1282.46	1260.82	1312.82	1265.14	1215.51	1299.82
0.6546	1256.26	1236.59	1281.84	1240.69	1200.87	1270.36	1236.61	1216.50	1262.34	1220.27	1180.21	1250.57
0.7559	1214.18	1198.17	1233.98	1201.37	1172.14	1224.62	1194.46	1178.08	1214.36	1181.04	1151.68	1204.80
0.8840	1162.07	1153.50	1172.67	1155.18	1140.86	1168.35	1142.22	1133.46	1152.88	1135.02	1120.65	1148.43
1.0000	1116.45	1116.45	1116.45	1116.45	1116.45	1116.45	1096.47	1096.47	1096.47	1096.47	1096.47	1096.47

Table-2
Percentage deviations and interaction parameters (α) for diethyl carbonate + aniline at different temperatures

x_1	$\%u_{NR}$	$\%u_{IR}$	$\%u_{IMR}$	$\%u_{JR}$	$\%u_R$	α	$\%u_{NR}$	$\%u_{IR}$	$\%u_{IMR}$	$\%u_{JR}$	$\%u_R$	α
	293.15 K						298.15 K					
0.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
0.0730	0.33	-0.63	0.20	1.72	-0.46	0.0040	0.35	-0.64	0.22	1.79	-0.46	0.0045
0.1652	0.66	-1.30	0.38	3.15	-0.88	0.0077	0.70	-1.32	0.44	3.28	-0.88	0.0088
0.2537	0.94	-1.74	0.56	4.00	-1.15	0.0113	1.01	-1.75	0.65	4.19	-1.13	0.0131
0.3387	1.16	-2.00	0.72	4.46	-1.31	0.0145	1.22	-2.03	0.80	4.63	-1.31	0.0162
0.4432	1.37	-2.11	0.89	4.63	-1.37	0.0181	1.44	-2.14	0.98	4.81	-1.37	0.0199
0.5468	1.38	-2.11	0.91	4.36	-1.32	0.0185	1.45	-2.14	1.00	4.53	-1.32	0.0203
0.6546	1.35	-1.85	0.93	3.83	-1.10	0.0188	1.41	-1.88	1.00	3.97	-1.10	0.0204
0.7559	1.13	-1.48	0.80	3.01	-0.84	0.0162	1.18	-1.51	0.86	3.12	-0.84	0.0175
0.8840	0.63	-0.83	0.45	1.59	-0.53	0.0091	0.66	-0.85	0.48	1.64	-0.53	0.0097
1.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
	303.15 K						308.15 K					
0.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
0.0730	0.37	-0.65	0.25	1.87	-0.46	0.0050	0.39	-0.66	0.28	1.95	-0.46	0.0056
0.1652	0.73	-1.34	0.49	3.42	-0.88	0.0098	0.77	-1.36	0.54	3.56	-0.89	0.0109
0.2537	1.06	-1.77	0.72	4.36	-1.13	0.0146	1.09	-1.82	0.77	4.50	-1.16	0.0156
0.3387	1.28	-2.07	0.88	4.81	-1.31	0.0178	1.34	-2.10	0.96	5.00	-1.32	0.0195
0.4432	1.51	-2.18	1.07	5.00	-1.37	0.0217	1.57	-2.22	1.16	5.18	-1.38	0.0236
0.5468	1.52	-2.18	1.09	4.70	-1.33	0.0221	1.58	-2.22	1.17	4.87	-1.33	0.0239
0.6546	1.47	-1.92	1.08	4.11	-1.11	0.0220	1.53	-1.95	1.16	4.26	-1.12	0.0236
0.7559	1.23	-1.54	0.93	3.23	-0.85	0.0188	1.28	-1.57	0.99	3.35	-0.86	0.0201
0.8840	0.69	-0.87	0.52	1.70	-0.53	0.0105	0.71	-0.88	0.56	1.76	-0.54	0.0112
1.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
	313.15 K						318.15 K					
0.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
0.0730	0.41	-0.67	0.30	2.03	-0.47	0.0061	0.44	-0.67	0.34	2.12	-0.46	0.0069
0.1652	0.81	-1.38	0.59	3.70	-0.89	0.0120	0.84	-1.40	0.65	3.84	-0.90	0.0131
0.2537	1.14	-1.86	0.84	4.68	-1.17	0.0170	1.19	-1.89	0.91	4.85	-1.18	0.0185
0.3387	1.40	-2.14	1.05	5.19	-1.33	0.0212	1.46	-2.18	1.13	5.38	-1.34	0.0230
0.4432	1.64	-2.26	1.25	5.37	-1.39	0.0254	1.71	-2.30	1.34	5.56	-1.40	0.0273
0.5468	1.65	-2.27	1.26	5.04	-1.34	0.0257	1.72	-2.31	1.35	5.22	-1.35	0.0276
0.6546	1.59	-2.00	1.24	4.41	-1.12	0.0253	1.65	-2.04	1.32	4.56	-1.13	0.0270
0.7559	1.34	-1.60	1.05	3.46	-0.86	0.0214	1.39	-1.64	1.12	3.58	-0.87	0.0229
0.8840	0.74	-0.90	0.59	1.83	-0.54	0.0120	0.77	-0.92	0.63	1.89	-0.54	0.0127
1.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000