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Application of Speed of Sound Relations to Binary System at Different Temperatures

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ABSTRACT

Speed of sound and density of the binary liquid mixtures of anisaldehyde with nonanol have been measured at temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K over the entire mole fraction range. The theoretical values of ultrasonic velocity were evaluated using Nomoto's relation (U_N), ideal mixing relation (U_{imx}), impedance relation (U_{Imp}), Rao's specific velocity relation (U_R) and Jungie's relation (U_J). The molecular interaction parameter (χ) has been evaluated from the experimental and theoretical velocity values. The variation of this interaction parameter with the mole fraction has been discussed in terms of molecular interactions.

Keywords: Anisaldehyde, alcohols, Nomoto's relation, Junjie's relation, Impedance relation.

INTRODUCTION

In recent years, measurement of speed of sound has been playing an important role in determining the physico-chemical properties of liquid mixtures [1,2]. Interest in studying the intermolecular interactions in liquid mixtures has been increasing in the last two decades and number of experimental and theoretical techniques has been used to identify the interactions between the molecules in binary and ternary liquid mixtures. Several researchers carried out ultrasonic investigations and correlated the experimental values of speed of sound with the theoretical relations of Nomoto [3], ideal mixing relation [4], impedance relation [5], Rao's specific velocity relation [6] and Junjie's relation [7] and the results are interpreted in terms of molecular interactions.

Here we present the theoretically evaluated values of speed of sound along with experimental values and % deviations at temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K over the entire mole fraction range. Based on earlier studies [8,9] an attempt has been made to study the molecular interactions from the values of U^2/U^2_{imx}.

MATERIALS AND METHODS

The chemicals used were of AnalaR grade and obtained from Merck and were used directly without further purification. The purity of the sample was checked by comparing experimental values of density and speed of sound with the available literature values. To prepare the mixtures of required proportion Job's method of continuous variation was used and the prepared mixtures were preserved in well-Stoppard conical flasks.

An ultrasonic pulse echo interferometer (Mittal Enterprises, India; Model: F-80X) was used to measure the speed of sound. The measurements of speed of sound were made at a fixed frequency of 3MHz. The speed of sound has an accuracy of ±0.5 ms^{-1}. The temperature stability was maintained within ± 0.01 K by circulating water around the liquid cell from thermostatically controlled constant temperature water bath. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle. An electronic balance (Shimadzu AUY 220, Japan) with a precision of ±0.1 mg was used for the mass measurements.

Different theoretical relations [10] are used to calculate the speed of sound and the results are compared with the experimental values.

RESULTS AND DISCUSSION

The experimental values of speed of sound along with the theoretical values of Nomoto relation, Ideal mixing relation, impedance relation, Rao's specific velocity relation and Junjie's relation for the binary mixtures over the entire mole fraction range and at temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K are given in table 1. The % deviation values along with χ values at different temperatures are given in table 2.

Table 1. Experimental and theoretical values of velocities (m/s) in anisaldehyde + nonanol system at different temperatures

x_1	U_{exp}	U_N	U_{imx}	U_{Imp}	U_R	U_J
303.15 K						
0.0000	1348.42	1348.42	1348.42	1348.42	1348.42	1348.42
0.1389	1361.05	1379.40	1381.49	1408.35	1338.43	1356.18
0.2664	1379.99	1410.85	1414.52	1458.38	1368.48	1368.84
0.3836	1395.78	1442.77	1447.52	1500.78	1389.78	1386.43
0.4919	1415.00	1475.16	1480.53	1537.18	1407.66	1409.10
0.5922	1428.00	1508.02	1513.55	1568.76	1414.23	1437.11
0.6854	1449.47	1541.36	1546.60	1596.42	1442.81	1470.89
0.7721	1486.00	1575.18	1579.71	1620.85	1501.52	1511.03
0.8531	1524.00	1609.49	1612.90	1642.59	1559.51	1558.38
0.9289	1583.00	1644.28	1646.18	1662.05	1597.27	1614.04
1.0000	1679.57	1679.57	1679.57	1679.57	1679.57	1679.57
308.15 K						
0.0000	1335.78	1335.78	1335.78	1335.78	1335.78	1335.78
0.1389	1352.00	1365.82	1371.01	1393.98	1341.07	1343.07
0.2664	1367.36	1396.32	1405.44	1442.55	1368.37	1355.18
0.3836	1383.15	1427.26	1439.11	1483.69	1382.80	1372.14
0.4919	1398.95	1458.67	1472.07	1518.99	1394.03	1394.08
0.5922	1411.57	1490.54	1504.35	1549.61	1404.82	1421.26
0.6854	1430.53	1522.88	1536.01	1576.42	1436.46	1454.07
0.7721	1452.63	1555.68	1567.07	1600.08	1472.65	1493.10
0.8531	1488.00	1588.96	1597.56	1621.14	1510.27	1539.14
0.9289	1559.00	1622.71	1627.51	1639.98	1564.01	1593.26
1.0000	1656.95	1656.95	1656.95	1656.95	1656.95	1656.95
313.15 K						
0.0000	1310.53	1310.53	1310.53	1310.53	1310.53	1310.53
0.1389	1332.63	1340.13	1345.29	1368.20	1320.88	1317.59
0.2664	1348.42	1370.20	1379.27	1416.28	1342.07	1329.40
0.3836	1361.05	1400.74	1412.52	1456.97	1360.25	1346.01

0.4919	1379.99	1431.75	1445.08	1491.86	1382.21	1367.56
0.5922	1395.78	1463.24	1476.99	1522.10	1389.72	1394.32
0.6854	1417.89	1495.21	1508.29	1548.57	1416.63	1426.69
0.7721	1436.84	1527.67	1539.01	1571.93	1451.51	1465.27
0.8531	1473.00	1560.62	1569.19	1592.69	1486.92	1510.87
0.9289	1532.00	1594.06	1598.84	1611.27	1532.21	1564.61
1.0000	1628.00	1628.00	1628.00	1628.00	1628.00	1628.00
			318.15 K			
0.0000	1297.89	1297.89	1297.89	1297.89	1297.89	1297.89
0.1389	1314.00	1326.82	1332.01	1354.43	1306.01	1304.57
0.2664	1329.47	1356.21	1365.33	1401.52	1325.39	1315.96
0.3836	1348.42	1386.06	1397.92	1441.36	1343.57	1332.09
0.4919	1365.00	1416.39	1429.80	1475.49	1374.76	1353.09
0.5922	1380.11	1447.19	1461.04	1505.07	1387.71	1379.23
0.6854	1395.78	1478.48	1491.65	1530.94	1410.33	1410.92
0.7721	1417.89	1510.25	1521.67	1553.77	1441.78	1448.74
0.8531	1451.00	1542.51	1551.15	1574.05	1467.82	1493.48
0.9289	1509.78	1575.27	1580.09	1592.20	1520.17	1546.24
1.0000	1608.53	1608.53	1608.53	1608.53	1608.53	1608.53

Table 2. Comparison of Percentage deviations and interaction parameters (χ) for the system at different temperatures**.**

x_1	% U_N	% U_{imx}	% U_{Imp}	% U_R	% U_J	χ
			303.15 K			
0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	1.0000
0.1389	-1.3485	-1.5017	-3.4749	1.6622	0.3577	1.0303
0.2664	-2.2364	-2.5020	-5.6804	0.8339	0.8078	1.0507
0.3836	-3.3666	-3.7071	-7.5230	0.4299	0.6698	1.0755
0.4919	-4.2515	-4.6308	-8.6347	0.5184	0.4173	1.0948
0.5922	-5.6037	-5.9906	-9.8573	0.9641	-0.6378	1.1234
0.6854	-6.3397	-6.7012	-10.1385	0.4596	-1.4776	1.1385
0.7721	-6.0016	-6.3064	-9.0749	-1.0443	-1.6847	1.1301
0.8531	-5.6095	-5.8333	-7.7813	-2.3302	-2.2556	1.1201
0.9289	-3.8713	-3.9911	-4.9934	-0.9013	-1.9607	1.0814
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
			308.15 K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
0.1389	-1.0223	-1.4063	-3.1052	0.8085	0.6604	1.0283
0.2664	-2.1176	-2.7849	-5.4989	-0.0739	0.8904	1.0565
0.3836	-3.1894	-4.0457	-7.2690	0.0251	0.7959	1.0826
0.4919	-4.2691	-5.2265	-8.5807	0.3514	0.3482	1.1073
0.5922	-5.5946	-6.5730	-9.7789	0.4782	-0.6862	1.1358
0.6854	-6.4555	-7.3734	-10.1980	-0.4143	-1.6457	1.1529
0.7721	-7.0942	-7.8778	-10.1509	-1.3782	-2.7861	1.1638
0.8531	-6.7849	-7.3626	-8.9474	-1.4966	-3.4367	1.1527
0.9289	-4.0868	-4.3944	-5.1945	-0.3216	-2.1977	1.0898
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
			313.15 K			
0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	1.0000
0.1389	-0.5630	-0.9502	-2.6692	0.8814	1.1290	1.0191
0.2664	-1.6153	-2.2881	-5.0323	0.4707	1.4103	1.0463
0.3836	-2.9161	-3.7818	-7.0474	0.0587	1.1047	1.0771
0.4919	-3.7508	-4.7168	-8.1064	-0.1607	0.9005	1.0966
0.5922	-4.8331	-5.8184	-9.0502	0.4344	0.1048	1.1198
0.6854	-5.4532	-6.3758	-9.2164	0.0888	-0.6207	1.1316
0.7721	-6.3213	-7.1109	-9.4016	-1.0213	-1.9788	1.1473
0.8531	-5.9481	-6.5299	-8.1257	-0.9450	-2.5711	1.1349
0.9289	-4.0509	-4.3629	-5.1745	-0.0134	-2.1284	1.0892
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000

318.15 K						
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
0.1389	-0.9754	-1.3703	-3.0767	0.6079	0.7176	1.0276
0.2664	-2.0110	-2.6975	-5.4197	0.3071	1.0161	1.0547
0.3836	-2.7915	-3.6707	-6.8924	0.3598	1.2113	1.0748
0.4919	-3.7647	-4.7476	-8.0948	-0.7151	0.8725	1.0972
0.5922	-4.8606	-5.8638	-9.0543	-0.5504	0.0635	1.1207
0.6854	-5.9247	-6.8685	-9.6837	-1.0423	-1.0849	1.1421
0.7721	-6.5137	-7.3197	-9.5831	-1.6851	-2.1756	1.1518
0.8531	-6.3067	-6.9018	-8.4805	-1.1590	-2.9276	1.1428
0.9289	-4.3376	-4.6569	-5.4591	-0.6885	-2.4151	1.0953
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000

It is not always true to assume the shape of molecules as sphere. In Nomoto's theory it is supposed that the volume does not change on mixing. So, no interaction between the components of liquid mixtures has been taken into account. In ideal mixing relation it is assumed that the ratio of specific heats of ideal mixtures and the volumes are also equal. No molecular interactions are taken into account. In Collision factor theory it is assumed that the molecules as real nonelastic substances, which is not true. When two liquids are mixed, the interactions between the molecules of the two liquids takes place because of presence of various types of forces such as hydrogen bonding, dipole-dipole, dipole-induced dipole, dispersive forces and charge transfer [11,12]. The deviations of theoretical values of speed of sound from the experimental values shows the existence molecular interactions between the unlike molecules in liquid mixtures. From table 2 it is observed that the theoretical values of speed of sound calculated from various theories show deviations from experimental values. The reason for this may be due to the limitations and approximations incorporated in these theories.

In general, the predictive ability of various ultrasonic theories depends upon the strength of interactions that exist in a binary system. More deviations are observed in case of strong interactions and fewer deviations are observed in case of week interactions.

From table 2 it is observed that there is a good agreement between experimental and theoretical values calculated from Rao's specific velocity method and Junjie's relation. Here Rao's method provides the best results than the results of Junjie's relation at all temperatures. However it is also observed from the same table that there are more deviations in Nomoto's relation, Ideal mixing relation and impedance relation.
The percentage deviations of the speed of sound are both negative and positive. Such deviations indicate the nonideal behaviour of liquid mixtures. The ratio U^2_{exp}/U^2_{imx} is used as an important tool to measure the nonideality in the mixtures, especially in those cases where the properties other than speed of sound are not known. From the data it can be understood that, positive deviation in speed of sound are attributed to the molecular association, complex formations, whereas negative deviations indicate molecular dissociation of an associated species by the addition of solvent.

In the present system, U^2_{exp}/U^2_{imx} values are observed to be positive at all measured temperatures due to more complex formations between unlike molecules through hydrogen bonding. The values of interaction parameter observed from table 2 are positive. The positive values of interaction parameter represent strong interaction between the molecules of the mixture.

The deviations between theoretical and experimental value of speed of sound are observed to be decreased with increase of temperature [13]. The decrease in speed of sound values with increase in temperature is probably due to the fact that the thermal energy activates the molecule, which would increase the rate of association of unlike molecules [14].

APPLICATIONS

The observed positive and negative % deviations in different theories are useful to explain the intermolecular interactions present in the binary mixtures.

CONCLUSIONS

Speed of sound and density values are measured experimentally. The experimental value of speed of sound are compared with the theoretical values of Nomoto's relation, Van Deal ideal mixing relation, Impedance relation, Rao's relation and Junjie's relation. Out of five mixing relations, Rao's relation provides good results when compared with other relations.

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