JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

A STUDY OF CHI SQUARE TEST FOR GOODNESS OF FIT

Smt.Paled Maheshwari
Assistant Professor, Dept of Chemistry, Government First Grade College, Bidar, Karnataka, India

Abstract

Theoretical values of ultrasonic velocity in binary liquid mixture of anisic aldehyde cyclo hexane have been evaluated at 303.15,308.15,313,15 and 318.15 K using Nomoto's relation, ideal mixing relation (IMR) impedance dependence relation (IDR), Rao's velocity method (RVM) and Junjie's method (JM). The relative merits of these theoretical relations were examined by comparing the theoretical values of ultrasonic velocity with the values obtained experimentally. The validity of the theories was checked by applying the chi-squares test for goodness of fit.

Keywords: Ultrasonic Velocity, Anisic Aldehyde, cyclo hexane, Chi-Square Test.

1. Introduction

Chi Square Test is used to determine whether the experimental data is consistent with theoretical data. It is very useful in estimating the correctness of theories used to calculate ultrasonic velocities.

In recent years an increasing variety of research techniques are being employed to get an insight into the molecular behaviour of liquids. In the present stage of development, ultrasonic techniques are yielding fruitful results comparable with those of other methods in the elucidation of molecular mechanisms.

Measurement of sound velocity has been used for many years in connected with the determination of elastic and thermodynamic properties of gases, liquids and solids. Intimate relations between the values of sound velocity and chemical or structural characteristics of molecules of liquids or liquid mixtures have been found. This gives sound velocity the primary quantity in the molecular theory of liquids.

Theoretical evaluation of ultrasonic velocity in binary liquid mixtures and its comparison with the experimental values reflects the molecular interaction in liquid mixtures, which is very useful to build comprehensive theoretical model for liquids. Several researches [1-9] carried out investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with the theoretical relations like Nomoto's relation [10], ideal mixing relation (IMR) [11], impedance dependence relation (IDR) [12], Rao's velocity method (RVM) [13] and Junjie's method (JM) [14]. Further, the best suitable theory for the given studied system is also picked out by computing the average percentage error and Chi-Square test.

In the present investigation anisic aldehyde is mixed with cyclo hexane at different mole fractions to study the interactions between the component molecules. The results are explained and discussed in terms of molecular interactions present in the investigated systems.

Experimental

Anisic aldehyde, cyclo hexanol from Merk were purified as described in the literature [15, 16]. The pure chemicals were stored over activated 4Å molecular sieves to reduce water content before use.

The mixtures are prepard gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1\times 10^{-7}\,kg$ and stored in airtight bottles. The uncertainty on mole fraction is estimated to be 1×10^{-8}. It is ensured that the mixtures are properly mixed and the measurement of the required parameters was done within one day of preparation.

The densities, ρ_x of pure liquids and their mixtures are determined using a 10^{-5} m^3double-arm pycnometer, and the values from triplicate replication at each temperature are reproducible within $2\times 10^{-1}\,kgm^3$ 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.

Temperature control for the measurement of viscosity and density is achieved by using a microprocessor assisted circulating water bath. (Supplied by Mac. New Delhi) regulated to $\pm 0.01K$, using a proportional temperature controller. Adequate precautions were taken to minimize evaporation losses during the actual measurements.

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

3. Theoretical Considerations

Nomoto Equation

Rao [17] proposed the relation that the ratio of temperature coefficients of sound velocity U and molar volume V remains almost constant for pure liquids:

$$\left[(1/U)(dU/dT)\right]/\left[(1/V)(dV/dT)\right] = -3 \qquad \ldots(1)$$

where T is the absolute temperature.

Integration the above equation, we get

$$VU^{1/3} = const = M/\rho U^{1/3} = R \qquad \ldots(2)$$

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

$$M = (X_1M_1 + X_2M_2) \qquad \ldots(3)$$

where M_1 and M_2 are molecular weights of constituent components.

Simple manipulation yields the following relation

$$U = \left[(X_1R_1 + X_2R_2)/(X_1V_1 + X_2V_2)\right]^3 \quad (4)$$

The Van Dael and Vancel Equation

Van Dael [11] obtained the relation for ultrasonic velocity in liquid mixtures as

$$I/(M_1M_1 + X_2M_2) * 1/U_{\max}^2 = X_1/M_1U_1^2 + X_2/M_2U_2^2 \qquad \ldots(5)$$

where $U_{\max}$ is the ideal mixing ultrasonic velocity in liquid mixture. U_1 and U_2 are ultrasonic velocities in species.

The Impedance Relation

Impedance relation $U = \Sigma X_i Z / \Sigma X_i p_i \qquad \ldots(6)$

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

The Rao's Specific Velocity Method Relation

Rao's specific velocity method$^{1/4}$ $U = (\Sigma X_i r_i \rho)^3 \quad \ldots(7)$

where X_i mole fraction, U_i is the ultrasonic velocity, ρ_I is the density of the mixture, r_i is the Rao's specific sound velocity $= Ui^{1/3}/\rho_i$ and Z_i is the acoustic impedance.

The Junjie Equation

Junjie equation

$$U_f = \left(X_i M_1 / \rho_1 + X_2 M_2 / \rho_2 \right) / \left[\left\{ X_1 M_1 + X_2 M_2 \right\}^{1/2} \left\{ X_1 M_1 / \rho_i U_i^2 + X_2 M_2 / \rho_2 U_2^2 \right\}^{1/2} \right] \ldots(8)$$

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

Chi-Square Test for Goodness of Fit

According to Karl Pearson [19] Chi-square value is evaluated for the binary liquid mixtures under study using the formula

$$\chi^2_{i=1}^{N} = \Sigma\left(U_{mix(obs)} - U_{mix(cal)}{}^2 / U_{mix(cal)} \right) \qquad \ldots(10)$$

where *n* is the umber of data used.

4. Discussions

Anisic Aldehyde, also known as para methoxy benzaldehyde is slightly polar (CH = O group). Oxygen is more electronegative than carbon so it has a tendency to pull electrons in a carbon-oxygen bond towards itself. The experimental values of ultrasonic velocity for the system along with theoretical values and percentage deviations for Nomoto's Relation (U_{NR}). Vandeal Vangael Ideal Mixing Relation (U_{max}). Impedance Dependence Relation (U_i). Rao's specific velocity method (U_{Rao}) and Junjie's relation (U_j) are compared for the studied binary mixture. The agreement between theoretical velocities of Nomoto's relation in all the three binary systems suggests that *R* is additive property in all the three systems. It is observed that the experimental values show deviation with the theoretical values of ultrasonic velocities which confirms the existence of molecular interactions.

Table 1 shows the values of ultrasonic velocity computed by various theories along with experimental values (U). There are variations between the evaluated and experimental values. From the observed values of the binary system, there is a good agreement between theoretical and experimental values through junji's followed by Nomoto Relation.

On the whole, all the theoretical models fairly predicted ultrasonic velocities, are reasonably close to the experimental values for 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 system [20]. In general the predictive ability of various ultrasonic theories depends upon the strength of interactions that exist in a binary system. In case strong interactions exist 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 present, and the average absolute percentage relative deviation is small in systems where the interactions are less or nil.

Table 8.3.13(a)

Experimental velocities (U/m-sec^{-3}), theoretical velocities (Ux/m.sec^{-1}) for the system anisic aldehyde (AA)+Cyclo Hexene (CHe)

X_i	**U_{exp} ms^{-1}**	**U_{sn} ms^{-1}**	**U_{ims} ms^{-1}**	**U_{in} ms^{-1}**	**U_R ms^{-1}**	**U_3 ms^{-1}**
0.0000	1252.20	1252.20	1252.20	1252.20	1252.20	1252.20
0.0856	1256.89	1279.52	1251.09	1285.92	1317.12	1261.87
0.1741	1265.24	1307.23	1253.77	1318.47	1374.55	1274.53
0.2654	1276.90	1335.35	1260.70	1349.93	1424.40	1290.46
0.3598	1292.70	1363.86	1272.51	1380.34	1467.93	1309.99
0.4574	1312.84	1392.78	1290.15	1409.76	1505.90	1333.62
0.5584	1339.33	1422.10	1314.92	1438.23	1537.43	1361.94
0.6630	1372.61	1451.83	1348.75	1465.79	1559.58	1395.77
0.7713	1415.84	1481.97	1394.53	1492.50	1568.24	1436.22
0.8835	1471.54	1512.53	1456.87	1518.39	1561.49	1484.77
1.0000	1543.50	1543.50	1543.50	1543.50	1543.50	1543.50
	χ^2	6.489	14.384	31.575	287.668	0.245

308.15K						
0.0000	1224.80	1224.80	1224.80	1224.80	1224.79	1224.80
0.0856	1228.64	1252.17	1252.17	1258.62	1287.01	1234.55
0.1741	1236.84	1279.94	1279.94	1291.27	1340.53	1247.28
0.2654	1248.57	1308.11	1308.11	1322.83	1389.92	1263.24
0.3598	1264.06	1336.70	1336.70	1353.33	1433.51	1282.80
0.4574	1284.22	1365.70	1365.70	1382.84	1469.78	1306.44
0.5584	1310.35	1395.11	1395.11	1411.40	1500.23	1334.79
0.6630	1343.91	1424.95	1424.95	1439.05	1522.12	1368.67
0.7713	1386.78	1455.21	1455.21	1465.84	1533.57	1409.21
0.8835	1442.18	1485.89	1485.89	1491.82	1532.02	1457.93
1.0000	1517.00	1517.00	1517.00	1517.00	1517.00	1517.00
	χ^2	7.369	15.582	33.652	197.917	0.353

313.15K						
0.0000	1196.60	1196.60	1196.60	1196.60	1196.60	1196.00
0.0856	1201.07	1225.74	1196.51	1232.78	1255.85	1207.26
0.1741	1210.32	1255.35	1200.19	1267.72	1309.66	1220.95
0.2654	1222.99	1285.43	1208.14	1301.49	1358.80	1238.00
0.3598	1239.37	1315.98	1221.05	1334.14	1403.13	1258.80
0.4574	1260.70	1347.01	1239.90	1365.72	1441.15	1283.90

0.5584	1288.48	1378.52	1266.12	1396.30	1474.14	1313.99
0.6630	1324.14	1410.51	1301.80	1425.91	1497.82	1350.03
0.7713	1369.35	1442.98	1350.16	1454.60	1511.80	1393.30
0.8835	1427.83	1475.94	1416.37	1482.42	1518.56	1445.57
1.0000	1509.40	1509.40	1509.40	1509.40	1509.40	1509.40
	χ^2	7.722	17.273	40.364	2149.956	0.178

318.15K						
0.0000	1169.60	1189.00	1169.60	1169.60	1169.60	1160.60
0.0856	1174.19	1217.08	1169.96	1206.87	1228.01	1180.57
0.1741	1184.25	1245.64	1174.08	1242.86	1278.53	1191.82
0.2654	1197.30	1274.68	1182.46	1277.65	1327.34	1212.35
0.3598	1214.20	1304.22	1195.83	1311.30	1372.11	1233.71
0.4574	1236.20	1334.25	1215.19	1343.85	1410.87	1239.45
0.5584	1264.70	1364.77	1242.03	1375.37	1445.20	1290.31
0.6630	1301.20	1395.81	1278.51	1405.90	1470.34	1327.32
0.7713	1347.60	1427.35	1327.99	1435.49	1486.46	1371.85
0.8835	1407.74	1459.42	1395.96	1464.17	1496.22	1425.31
1.0000	1492.00	1492.00	1492.00	1492.00	1492.00	1492.00
	χ^2	7.886	17.975	43.916	2328.091	0.191

5. References

1. Rambabu, C., Sandhya Sri, P.B., and Zareena Begum, International Scholarly Research Network ISRN Physical Chemistry Volume 2012, Article ID 934429, 12 pages doi: 10.5402/2012/943429.

2. Rambabu, C., Rama Rao, G.V., Viswanatha Sarma, A., and Siva Rama Krishna, J., (2005) Theoretical evaluation of ultrasonic velocities in binary liquid mixtures of o-chlorophenol at different temperatures, Indian Journal of Pure and Applied Physics May 43, 345.

3. Santhi, N., Sabarathinam, P.L. Emayavaram, ban, M. Gopi, C. and Manivannan, C., (2010). Molecular Interaction Studies in Binary Liquid Mixtures from Ultrasonic Data, E.J. or Chemistry, 7(2) 648.

4. Singh, J., Mohanthy G.C., and Acharya, S. (2013). Evaluation of ultrasonic parameters in binary mixtures of ethyl methyl ketone and alcohols vis – a – vis molecular interaction, J of Pure and Appl. Physics, 51, 542.

5. Raju, K. and Karpagavalli, K. (2009): Theoretical evaluation of ultrasonic velocity in binary mixtures of aprotic and inert solvents. Journal of convergence in engineering, Technology and science Vol 1 (1) pp 31.

6. Sahu, S., Nath, G., and Paikaray, R. (2012). Study on Molecular Interactions in Binary Mixture at Variable Frequencies Using Ultrasonic Technique Research Journal of Chemical Sciences Vol. 2(11), 64.

7. Yuva Rani and S. Punitha (2009). Theoretical Prediction of Ultrasonic Velocity in Organic Liquid Mixtures, E.J. of Chemistry, 6 (SI), S235.

8. Santhi N., Sabarathinam, P.L. Madhumitha, J. Alamelumangai, G. Emayavaramban. M. (2013). Theoretical Evaluation of Ultrasonic Velocity in Binary Liquid Mixtures of Alcohols [S] + Benzene, International Letters of Chemistry, Physics and Astronom, 2 18

9. Indhumathi, M. Meenakshi, G. Priyadharshini, VJ., Kayalvizhi, R and Thiyagaraj. S. (2013). Research Journal of Pharmaceutical, Biological and Chemical Sciences, April – June RJPBCS Volume 4 Issue 2 Page No. 1382.

10. Nomoto O (1958) Empirical Formula for Sound Velocity in Liquid Mixtures J. Phys Soc 13: 1528-1532.