Experimental and Theoretical Studies of Ultrasonic Velocity in Binary Liquid Mixtures of Ethyl Benzoate

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Received 01 September 2011; Accepted 11 September 2011

Abstract: Ultrasonic velocity is measured at 2MHz frequency in the binary mixtures of Ethyl Benzoate with 1-Propanol, 1-Butanol, 1-Pentanol and theoretical values of ultrasonic velocity have been evaluated at 303K using Nomoto's relation, Impedance relation, Ideal mixture relation, Junjie's method and free length theory. Theoretical values are compared with the experimental values and the validity of the theories is checked by applying the chi-square test for goodness of fit and by calculating the average percentage error (APE). A good agreement has been found between experimental and Nomoto's ultrasonic velocity.

Keywords: Ultrasonic velocity, Binary mixtures and Theoretical prediction.

Introduction

Measurement of ultrasonic velocity gives the valuable information about the physicochemical behavior ^{1, 2} of the liquid and liquid mixtures. Several relations, semi-empirical formulas and theories are available for the theoretical computation of ultrasonic velocity in liquid and liquid mixtures³⁻⁷. In continuation of our dielectric work⁸⁻¹⁰ we report the ultrasonic velocity evaluated using Nomoto's relation³, Impedance relation⁴, Ideal mixture relation⁵, Junjie's method⁶ and free length theory⁷ for the binary mixtures of Ethyl benzoate with 1-Propanol, 1-Butanol, 1-Pentanol. Further, the best suitable theory for the given molecular system under study is also picked out by calculating the average percentage error and chi-square test.

Experimental

The compounds Ethyl benzoate, 1-Propanol, 1-Butanol, 1-Pentanol of 99% AR grade were supplied by Merck Co. Inc., Germany. The ultrasonic velocity was measured at 303K using a single crystal ultrasonic interferometer (M/s Mittal Enterprises, India) operating at a

frequency of 2 MHz with an accuracy of ± 0.1 m/s. The density was measured at 303K using specific gravity bottle method by the standard procedure.

Theory

The following relations/theories are used for the prediction of ultrasonic velocity in the binary liquid mixtures.

Nomoto's relations (NOM)

$$U_{\text{NOM}} = \left[\frac{X_1 R_1 + X_2 R_2}{X_1 V_1 + X_2 V_2} \right]^3$$

where, Molar sound velocity, $R_1 = \frac{m_1}{d_1} U_1^{1/3}$; $R_2 = \frac{m_2}{d_2} U_2^{1/3}$

Molar volume $V_1 = \frac{m_1}{d_1}$; $V_2 = \frac{m_2}{d_2}$

Ideal mixture relation (IMR)

$$U_{\text{IMR}} = \left[\frac{1}{X_1 m_1 + X_2 m_2} \right]^{1/2} \left[\frac{X_1}{m_1 U_1^2} + \frac{X_2}{m_2 U_2^2} \right]^{-1/2}$$

Junjie's method(JM)

$$U_{\text{JM}} = \left[\frac{X_1 V_1 + X_2 V_2}{(X_1 m_1 + X_2 m_2)^{1/2}} \right] \left[\frac{X_1 V_1}{d_1 U_1^2} + \frac{X_2 V_2}{d_2 U_2^2} \right]^{-1/2}$$

Impedance Relation (IMP)

$$U_{\text{IMP}} = \frac{X_1 Z_1 + X_2 Z_2}{X_1 \rho_1 + X_2 \rho_2}$$

Free length theory (FLT)

$$U_{\text{CFT}} = \frac{K}{L_{f \text{ mix}} d_{\text{exp}}^{1/2}}$$

Where, $L_{f \text{ mix}} = 2 \left[\frac{V_m - (X_1 V_{01} + X_2 V_{02})}{X_1 V_1 + X_2 V_2} \right]$

Molar volume at absolute zero, $V_{01} = V_1 \frac{U_1}{U_\infty}$; $V_{02} = V_2 \frac{U_2}{U_\infty}$

Surface area per mole, $Y_1 = \frac{2(V_1 - V_{01})}{L_{f1}}$; $Y_2 = \frac{2(V_2 - V_{02})}{L_{f2}}$

Where, 1, 2, represents the first and second component of the liquid mixture and the other symbols have their usual meanings.

Results and Discussion

The experimental values along with the values calculated theoretically using Nomoto's relation, collision factor theory, free length theory, ideal mixture relation and Junjie's method for the systems Ethyl benzoate+1-propanol, Ethyl benzoate+1-butanol and Ethyl benzoate+1-pentanol at 303K are given in Table 1. The validity of the theories is checked by applying Chi-square test and by calculating average percentage error.

Chi-square test for goodness of fit

According to Karl Pearson¹¹, the Chi-square value is calculated using the formula,

$$(\chi^2) = \sum_{i=1}^n \frac{(U_{mix(obs)} - U_{mix(cal)})^2}{U_{mix(cal)}}$$

For (n-1) degrees of freedom, where, n is the number of data used.

Average percentage error (APE)

The average percentage Error¹² is calculated using the relation,

$$APE = \frac{1}{n} \sum \frac{(U_{mix(obs)} - U_{mix(cal)})}{U_{mix(obs)}} \times 100\%$$

Where, n- number of data used.

$U_{mix(obs)}$ = experimental values of ultrasonic velocities.

$U_{mix(cal)}$ = computed values of ultrasonic velocities.

It can be seen from Table 1 that the theoretical values of ultrasonic velocity computed by various theories show deviation from experimental values. The predictive abilities of various ultrasonic theories depend upon the strength of interaction prevailing in a system. These theories generally fail to predict accurately the ultrasonic velocities where strong interactions are supposed to exist.

Table 1. Experimental and computed values of *Ultrasonic velocity* for different systems at 303K.

X_1	U_{exp} ms^{-1}	U_{NOM} ms^{-1}	U_{IMR} ms^{-1}	U_{JM} ms^{-1}	U_{IMP} ms^{-1}	U_{FLT} ms^{-1}
Ethyl benzoate + 1-Propanol						
0.0000	1189.2	1189.2	1189.2	1189.2	1189.2	1189.2
0.0548	1196.0	1196.0	1201.3	1200.8	1200.2	1196.0
0.1155	1212.4	1212.4	1213.5	1214.4	1211.9	1212.4
0.1829	1229.3	1229.3	1226.8	1229.4	1224.5	1229.3
0.2583	1245.4	1245.4	1239.0	1244.1	1238.0	1245.4
0.3431	1261.4	1261.4	1251.7	1261.3	1252.5	1261.4
0.4393	1278.2	1278.2	1266.4	1275.9	1268.2	1278.2
0.5493	1294.3	1294.3	1282.6	1293.9	1285.1	1294.3
0.6763	1311.2	1311.2	1299.5	1310.9	1303.5	1311.2
0.8246	1328.0	1328.0	1320.8	1329.2	1323.5	1328.0
1.0000	1345.4	1345.4	1345.4	1345.4	1345.4	1345.4
APE		0.0000	8.0371	-0.0282	0.3455	0.0000
Chi Square		0.0000	143.0694	0.0295	0.3474	0.0000

Ethyl benzoate + 1-Butanol						
0.0000	1228.4	1228.4	1228.4	1228.4	1228.4	1228.4
0.0664	1236.8	1236.8	1212.5	1232.3	1238.3	1236.8
0.1379	1248.1	1248.1	1199.5	1246.7	1248.5	1248.1
0.2152	1259.8	1259.8	1189.7	1259.4	1259.1	1259.8
0.2990	1271.6	1271.6	1183.8	1270.8	1270.0	1271.6
0.3901	1284.0	1284.0	1182.7	1284.6	1281.4	1284.0
0.4897	1294.4	1294.4	1187.9	1296.7	1293.2	1294.4
0.5988	1305.3	1305.3	1201.4	1309.7	1305.5	1305.3
0.7190	1316.3	1316.3	1226.9	1321.0	1318.3	1316.3
0.8520	1325.8	1325.8	1270.8	1335.8	1331.6	1325.8
APE		0.0000	0.0000	4.8504	- 0.1003	-0.0258
Chi Square		0.0000	49.2197	0.1289	0.0384	0.0000
Ethyl benzoate + 1-Pentanol						
1.0000	1345.4	1345.4	1345.4	1345.4	1345.4	1345.4
0.0000	1252.4	1252.4	1252.4	1252.4	1252.4	1252.4
0.0774	1263.0	1263.0	1243.5	1258.3	1261.4	1263.0
0.1587	1275.6	1275.6	1237.0	1268.3	1270.6	1275.6
0.2444	1287.6	1287.6	1233.3	1276.9	1279.7	1287.6
0.3347	1298.9	1298.9	1232.6	1288.7	1288.9	1298.9
0.4301	1310.0	1310.0	1235.6	1298.3	1298.2	1310.0
0.5309	1315.6	1315.6	1243.0	1307.4	1307.5	1315.6
0.6378	1323.6	1323.6	1255.7	1318.1	1316.9	1323.6
0.7511	1330.3	1330.3	1275.3	1329.1	1326.3	1330.3
0.8717	1338.0	1338.0	1304.1	1341.1	1335.8	1338.0
1.0000	1345.4	1345.4	1345.4	1345.4	1345.4	1345.4
APE		0.0000	3.3527	0.3963	0.3982	0.0000
Chi Square		0.0000	23.1024	0.4195	0.3545	0.0000

Table 1 shows that the Chi-square value and APE value are minimum for Nomoto's relation and Free length theory than those obtained by other theories. An important reason for deviation from experimental values of ultrasonic velocity is that the molecular association

effects are not taken into account in these theories. When two liquids are mixed, the interaction between the molecules of the two liquids takes place because of the presence of various forces like dispersive force, charge transfer, hydrogen bonding dipole-dipole and dipole-induced dipole interactions. Hence the observed deviation shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture¹³. Similar kinds of results were obtained by earlier workers¹⁴⁻¹⁶. The agreement between experimental and theoretical velocities of Nomoto relation in all the three binary systems, suggests that R is additive property in all the systems. Higher deviations are observed in some intermediate concentration range. This suggests the existence of strong tendency for the association between component molecules as a result of Hydrogen bonding^{17, 18}.

Conclusion

Ultrasonic velocities predicted using NOM, IMR, JM, IMP and FLT were compared with experimentally measured velocity values at 303K for the binary mixtures of Ethyl benzoate with 1-Propanol, 1-Butanol, 1-Pentanol. It may be concluded that Nomoto's relation is best suited for all the binary mixtures under study. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of intermolecular interactions in the systems studied.

Acknowledgements

The authors gratefully acknowledge the Project No.: ERIP/ER/0703688/M/01/1134, dated 31-03-2010 of DRDO and UGC DRS LEVEL III program No.F.530/1/DRS/2009 (SAP-I), dated 09-02-2009 New Delhi, to the department of Physics, ANU for providing financial assistance.

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