Theoretical Prediction of Ultrasonic Velocity in Binary Liquid Mixtures

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Abstract: Theoretical values of ultrasonic velocity in the binary mixtures of chlorobenzene with benzene have been evaluated at different temperatures from 303.15 K-323.15 K using Nomoto's relation, ideal mixture relation, Junjie's method, collision factor theory and free length theory. Theoretical values were compared with the experimental values and the validity of the theories was checked by applying the chi-square test for goodness of fit and by calculating the average percentage error (APE).

Keywords: Ultrasonic velocity, Binary mixtures, Theoretical prediction

Introduction

Measurement of ultrasonic velocity gives the valuable information about the physicochemical behavior of the liquid and liquid mixtures. Several relations, semi-empirical formula and theories are available for the theoretical computation of ultrasonic velocity in liquid and liquid mixtures¹⁻⁵. 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 ultrasonic velocity was measured at different temperatures from 303.15 K-323.15 K using a single crystal interferometer with a high degree of accuracy operating at a frequency of 2 MHz. The density was measured at different temperatures from 303.15 K-323.15 K using specific gravity bottle method by the standard procedure.

Theory

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

Nomoto's relations (NOM)

$$U_{\text{NOM}} = \left[\frac{X_1 R_1 + X_2 R_2}{X_1 V_1 + X_2 V_2} \right]^{\frac{1}{2}}$$

$$R_1 = \frac{m_1}{d_1} U_1^{\frac{1}{2}} ; R_2 = \frac{m_2}{d_2} U_2^{\frac{1}{2}}$$

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

Where, Molar sound velocity,

Molar volume

Ideal mixture relation (IMR)

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

Junjie's method (JM)

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

Collision factor theory (CFT)

$$U_{\text{CFT}} = U_{\infty} [(X_{1,1} S_{1,1} + X_{1,2} S_{1,2})(X_{1,1} B_{1,1} + X_{1,2} B_{1,2}) / V_1 m]$$

$$V_m = \frac{X_1 m_1 + X_2 m_2}{d_{\text{exp}}}$$

Where Molar volume of mixture,

Actual Volume,

$$B = \frac{4}{3} \pi r^3 N$$

Molecular radius,

$$r = \left[\frac{3b}{16\pi N} \right]^{\frac{1}{3}}$$

Vander Waal's constant,

$$b = \frac{m}{d} \left[1 - \frac{RT}{mU^2} \left(\frac{\sqrt{1 + mU^2}}{3RT} - 1 \right) \right]$$

Temperature dependent constant, $U_{\infty} = 1600$ m/sec, N is the Avagadro's number.

Free length theory (FLT)

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

Where,

$$L_{f_{\text{mix}}} = 2 \left[\frac{V_m - (X_1 V_{01} + X_2 V_{02})}{X_1 Y_1 + X_2 Y_2} \right]$$

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

$$Y_1 = \frac{2(V_1 - V_{01})}{L_{f_1}} ; Y_2 = \frac{2(V_2 - V_{02})}{L_{f_2}}$$

Surface area per mole,

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 system chlorobenzene + benzene at different temperatures 303.15 K-323.15 K

are given in Table 1. The validity of the theories was checked by applying Chi-square test and by calculating average percentage error.

Chi-square test for goodness of fit

According to Karl Pearson⁶, 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 Error⁷ 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 reason may be the limitations and approximations incorporated in these theories.

Table 1. Experimental and computed values of *Ultrasonic velocity* for chlorobenzene + benzene system at 303.15 K-323.15 K

X ₁	U _{exp} ms ⁻¹	U _{NOM} ms ⁻¹	U _{IMR} ms ⁻¹	U _{JM} ms ⁻¹	U _{CFT} ms ⁻¹	U _{FLT} ms ⁻¹
303.15 K						
0.0000	1281.21	1281.21	1281.21	1281.21	1281.21	1281.21
0.0887	1275.93	1278.01	1272.21	1275.43	1263.67	1212.05
0.1796	1271.26	1274.81	1264.37	1270.28	1247.96	1157.49
0.2728	1267.16	1271.61	1257.72	1265.73	1234.53	1116.27
0.3686	1263.59	1268.43	1252.28	1261.75	1223.83	1087.73
0.4668	1260.50	1265.24	1248.12	1258.35	1216.38	1071.86
0.5677	1257.83	1262.07	1245.30	1255.49	1212.74	1069.35
0.6714	1255.48	1258.89	1243.89	1253.18	1213.52	1081.79
0.7779	1253.38	1255.73	1244.02	1251.40	1219.39	1112.06
0.8874	1251.40	1252.57	1245.80	1250.14	1231.08	1165.12
1.0000	1249.41	1249.41	1249.41	1249.41	1249.41	1249.41
	APE	-0.2220	0.5963	0.1064	2.1129	9.2373
	Chi Square fit	0.0940	0.6738	0.0219	8.7186	182.0335
308.15 K						
0.0000	1258.23	1258.23	1258.23	1258.23	1258.23	1258.23
0.0887	1253.24	1255.48	1249.65	1252.87	1241.35	1195.06
0.1796	1248.88	1252.73	1242.23	1248.14	1226.27	1144.72
0.2728	1245.12	1249.99	1235.99	1244.01	1213.42	1106.37
0.3686	1241.93	1247.24	1230.98	1240.47	1203.26	1079.63
0.4668	1239.24	1244.51	1227.24	1237.49	1196.30	1064.65
0.5677	1237.01	1241.77	1224.84	1235.08	1193.10	1062.19
0.6714	1235.15	1239.04	1223.88	1233.22	1194.25	1073.81

Contd...

0.7779	1233.59	1236.31	1224.47	1231.90	1200.43	1102.24
0.8874	1232.20	1233.59	1226.74	1231.12	1212.37	1152.03
1.0000	1230.87	1230.87	1230.87	1230.87	1230.87	1230.87
	APE	-0.2511	0.5883	0.0883	2.0915	8.6826
	Chi Square fit	0.1177	0.6450	0.0150	8.4000	156.9854
313.15 K						
0.0000	1235.39	1235.39	1235.39	1235.39	1235.39	1235.39
0.0887	1230.70	1233.10	1227.24	1230.47	1219.19	1177.56
0.1796	1226.67	1230.82	1220.25	1226.17	1204.76	1131.08
0.2728	1223.26	1228.54	1214.43	1222.48	1192.52	1095.42
0.3686	1220.45	1226.26	1209.85	1219.37	1182.93	1070.43
0.4668	1218.19	1223.98	1206.54	1216.85	1176.49	1056.38
0.5677	1216.42	1221.71	1204.60	1214.89	1173.74	1054.07
0.6714	1215.07	1219.44	1204.10	1213.50	1175.29	1065.04
0.7779	1214.06	1217.17	1205.17	1212.66	1181.79	1091.84
0.8874	1213.29	1214.90	1207.95	1212.37	1193.97	1138.71
1.0000	1212.63	1212.63	1212.63	1212.63	1212.63	1212.63
	APE	-0.2816	0.5808	0.0696	2.0663	8.1749
	Chi Square fit	0.1449	0.6182	0.0094	8.0597	135.9120
318.15 K						
0.0000	1212.58	1212.58	1212.58	1212.58	1212.58	1212.58
0.0887	1208.58	1210.73	1204.84	1208.05	1197.02	1159.47
0.1796	1205.18	1208.88	1198.24	1204.16	1183.21	1116.48
0.2728	1202.36	1207.03	1192.83	1200.87	1171.55	1083.32
0.3686	1200.08	1205.19	1188.65	1198.18	1162.49	1059.98
0.4668	1198.29	1203.34	1185.75	1196.07	1156.54	1046.84
0.5677	1196.94	1201.49	1184.22	1194.54	1154.22	1044.73
0.6714	1195.94	1199.65	1184.15	1193.58	1156.13	1055.13
0.7779	1195.21	1197.80	1185.67	1193.19	1162.93	1080.48
0.8874	1194.65	1195.96	1188.93	1193.37	1175.32	1124.68
1.0000	1194.12	1194.12	1194.12	1194.12	1194.12	1194.12
	APE	-0.2487	0.6357	0.1152	2.1040	7.7713
	Chi Square fit	0.1118	0.7287	0.0243	8.2183	120.1387
323.15 K						
0.0000	1189.91	1189.91	1189.91	1189.91	1189.91	1189.91
0.0887	1186.42	1188.49	1182.56	1185.77	1174.96	1140.94
0.1796	1183.51	1187.06	1176.37	1182.26	1161.73	1101.07
0.2728	1181.17	1185.64	1171.35	1179.36	1150.62	1070.17
0.3686	1179.34	1184.21	1167.56	1177.07	1142.07	1048.37
0.4668	1177.98	1182.79	1165.06	1175.37	1136.59	1036.10
0.5677	1177.04	1181.37	1163.94	1174.26	1134.69	1034.22
0.6714	1176.43	1179.94	1164.29	1173.73	1136.97	1044.18
0.7779	1176.08	1178.52	1166.25	1173.79	1144.07	1068.28
0.8874	1175.86	1177.09	1169.98	1174.44	1156.71	1110.15
1.0000	1175.67	1175.67	1175.67	1175.67	1175.67	1175.67
	APE	-0.2409	0.6662	0.1369	2.1219	7.3990
	Chi Square fit	0.1033	0.7868	0.0336	8.2175	106.5289

Table 1 shows that the Chi-square value and APE value are minimum for Nomoto's relation than those obtained by other theories. However for the binary mixtures of chlorobenzene + benzene these values are minimum for JM. 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 mixture⁸. Similar kinds of results were obtained by earlier workers⁹⁻¹¹.

Conclusion

Ultrasonic velocities predicted using NOM, IMR, JM, CFT and FLT were compared with experimentally measured velocity values at different temperatures from 303.15 K- 323.15 K for the binary mixture of chlorobenzene+benzene. It may be concluded that nomoto's relation is best suited for the binary mixtures of chlorobenzene+benzene at all the temperatures. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of intermolecular interactions in the system studied.

References

1. Nomoto O, *J Phys Soc Jpn.*, 1958, **13**,1528.
2. Schaafs W, *Molekulara Kustik*, Springer, Verlag, Berlin-Gottinger-Heidelberg, 1963, Chapters 11 & 12.
3. Jacobson B, *Acta Chem Scand*, 1952, **6**, 1485.
4. Van Dael W and Vangeel E, *Proc Int Conf on calorimetry and thermodynamics*, Warasa, 1955, 555.
5. Junjie Z, *J China Univ Sci Tech.*, 1984, **14**, 298.
6. Pearson K, *Fundamentals of Mathematical Statistics*, Eds., Gupta S G and Kapoor V K, S Chand and Company, New Delhi, India, 1973, 903.
7. Jyh-Shing and Roger Jang, *IEEE Transactions on Systems, Man and Cybernetics*, 1993, **23(4)**, 665-685.
8. Rama Rao G V, Viswanatha Sarma A, Siva Rama Krishna J and Rambabu C, *Indian J Pure Appl Phys.*, 2005, **43**, 345-354.
9. Uvarani R and Punitha S, *E-J Chem.*, 2009, **6(S1)**, S235-S238.
10. Sumathi T and Abeetha K, *E-J Chem.*, 2011, **8(1)**, 252-256.
11. Vasantharani P, Muthu shailaja S, Kannappan A N, Ezhil Pavai R, *J Appl Sci.*, 2008, **8(12)**, 2329-2332.