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Prediction of ultrasonic velocities in pure liquids by theoretical methods at various temperatures

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ABSTRACT

Ultrasonic velocity is a fundamental property to study the physical and chemical behaviour of pure liquids and liquid mixtures. In this paper, we propose the new expressions for velocity of pure organic liquids. The sound velocity has been calculated by using experimental value of density and the literature values of critical volume (V_c) and critical temperature (T_c). The values of sound velocity have been evaluated theoretically using three new different methods. Further, the predicted theoretical velocities were compared with the experimental findings. This new expressions are shown to represent the experimental velocity data of 27 different polar organic liquids can be predicted within 5.81% to 10.7% absolute average deviation(AAD) for all temperature investigated.

Keywords: Velocity, Density, Critical temperature, Critical volume and Molar volume.

INTRODUCTION

Ultrasonic velocity in a medium is related to the binding forces between the molecules.

Ultrasonic velocities in liquid mixtures consisting of polar and non-polar components are of considerable importance in understanding the intermolecular interaction between component molecules and find applications in several industrial and technological processes [1-3]. According to physical concept of liquid model [4-6], molecules in the liquid state are so loosely packed as to leave some free space between them. The intermolecular free space and its dependent properties are related to intermolecular interactions and may reveal the information regarding the interaction, which may be occurring when the liquids are mixed together.

Parthasarathy [7,8] and Bergmann [9] from the measurement of ultrasound velocity in numerous organic liquids pointed out that,

1. Polar molecules have higher velocity (e.g.,) acetophenone, aniline, cyclohexanol, nitrobenzene, water etc.
2. In similar derivatives a change from light to heavy atom lower the velocity.
3. Long molecules give rise to higher velocities (e.g.,) Velocity in heptanes is higher than in hexane. The same is true of normal alcohols is less than corresponding alcohols.
4. Aromatics usually have higher velocities than the corresponding alphatics, although their densities are higher.

The theoretical evaluation of sound velocity in liquids and in liquid mixtures as a function of composition is of considerable interest. Also a comparison of theoretically obtained sound velocities with those of experimental is

found to be useful in knowing the thermodynamics of liquids and liquid mixtures and provides a better means to test the validity of the various empirical relations and theories.

Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids, binary and ternary mixture [10-14]. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [15] as well as strongly interacting components [16].

In recent years various theories [17-20] have been in use for computing ultrasonic velocity in liquid mixtures and the deviation in theoretical sound velocity from that of the experimental has been attributed mainly to the molecular interactions prevailing in liquid mixtures. The velocity gives information about the binding between the molecule and formation of complexes at various temperatures through molecular interactions.

EXPERIMENTAL SECTION

2. New theoretical approach of ultrasonic velocity

Attempts are made here in proposing a few new equations for predicting ultrasonic velocity in pure liquids. A flaw in the derivation of the Suryanarayana-Kuppusami [21] equation was noticed and a new formulation is presented here for the computation of free volume. By incorporating the compressibility state, Srivastava and Berkowitz [22] proposed a simple but nearly accurate method for estimating internal pressure of liquid systems. Here Jacobson's free length theory is used in the place of compressibility making the resulting model a totally predictive one.

Newly proposed Models

Since the ultrasonic velocity measurements in liquids are being used as a tool to probe into the properties of liquids, the prediction of ultrasonic velocities from pure liquid properties will be much use in scientific and engineering calculations. A few equations to predict ultrasonic velocities in pure liquids are proposed here.

Model 1

While discussing the calculations of free volume, Dewan et.al., [23] reported that

$$u = u_{\infty}\, b/\, V \qquad \text{_____ (1)}$$

Where $u_{\infty} = 1600\ ms^{-1}$
b, excluded volume = $V_c/4$
V_c = critical volume
V = molar volume

With $u_{\infty} = 1600\ ms^{-1}$ and $b = V_c/4$, eqn. (1) becomes

$$u = 400\ V_c\ /V \qquad \text{_____ (2)}$$

Eqn. (2) is simple and requires only molar volume and critical volume for the evaluation of ultrasonic velocity. Model 1 says that the ultrasonic velocity in a liquid is proportional to the ratio of critical molar volume to the molar volume of the liquid; the proportionality constant is 400 ms^{-1}. Model 1 can be considered as a form of collision factor theory.

Model 2

Rao [24,25] observed that the ratio of Rao's constant, R ($=u^{1/3}\ V$) to critical volume V_c, is nearly constant for most of the liquids and is equal to 3.6:

$$R/\ V_c \approx 3.6 \qquad \text{_____ (3)}$$

Putting $R = u^{1/3}\ V$ in eqn. (3), rearranging the resulting expression and simplifying one gets

$$U = (3.6\ V_c\ /V)^3 = 46.656(V_c\ /V)^3 \qquad \text{_____(4)}$$

Eqn.4 is Model 2 proposed in this work. According to Eqn.4, the ultrasonic velocity is linearly varying with the cube of the ratio, (V_c /V). The constant is 46.656 ms^{-1}.

Model 3
Rao [24,25] observed that the factor α, given by

$$\alpha = (R/ V_c)^{1/2} (M/T_c)^{1/6} \quad \text{_____(5)}$$

is even more nearly constant, (compared to R/ V_c = 3.6) 2.7 for normal liquids and lower, for associated liquids.

In corporating the definition of R in Eqn. (5) and putting α = 2.7 one obtains

$$u = (2.7)^3 (T_c/M)^{1/2} (V_c /V)^3 = 19.683 (T/M)^{1/2} (V_c /V)^3 \quad \text{_____(6)}$$

The critical temperature, critical volume and molar volume are the required data if one wants to use eqn.6 for predicting the ultrasonic velocity in a liquid. Like Model 2, Model 3 also says that u in a liquid is proportional to cube of the ratio (V_c /V). In addition $(T_c/M)^{1/2}$ is also a parameter to be considered in the evaluation of u through Model 3.

RESULTS AND DISCUSSION

The validity of different theoretical formulae is checked by percentage deviation at all the temperatures in pure liquid of 63 associated data points and is given in Table 1.

Table 1. Experimental and Ultrasonic velocities in Pure liquids Through Various Models

S.no	Associated Liquid	Ref	Temp.	Density	u_{Exp}	computed ultrasonic velocity, in ms^{-1} Through Model			Absolute % Deviation by using Model		
			K	$X10^{-3}Kgm^{-3}$	ms^{-1}	1	2	3	1	2	3
1	iso- Amyl alcohol	26	303.15	0.8052	1214.0	1202.1	1266.3	1369.7	0.98	4.31	12.83
2	Benzyl alcohol	27	303.15	1.0388	1506.7	1283.4	1540.9	1626.6	14.82	2.27	7.95
3			308.15	1.0343	1497.2	1277.8	1521.0	1605.5	14.65	1.59	7.23
4			313.15	1.0306	1487.1	1273.2	1504.7	1588.3	14.38	1.19	6.81
5			318.15	1.0266	1466.8	1268.3	1487.3	1569.9	13.53	1.40	7.03
6	n-Butyl acetate	28	303.15	0.8709	1184.0	1199.6	1258.3	1185.2	1.31	6.28	0.10
7	n-Butyl alcohol	29	303.15	0.8036	1230.0	1188.2	1223.0	1421.8	3.40	0.57	15.59
8			308.15	0.7992	1219.0	1181.7	1203.0	1398.6	3.06	1.31	14.73
9			313.15	0.7955	1206.0	1176.2	1186.4	1379.3	2.47	1.63	14.37
10			318.15	0.7917	1195.0	1170.6	1169.5	1359.6	2.04	2.14	13.77
11	iso- Butyl alcohol	30	303.15	0.7945	1185.0	1170.5	1169.0	1340.6	1.23	1.35	13.13
12			308.15	0.7927	1161.0	1167.8	1161.1	1331.5	0.59	0.01	14.69
13			313.15	0.7879	1150.2	1160.8	1140.1	1307.5	0.92	0.88	13.67
14			318.15	0.7840	1129.2	1155.0	1123.3	1288.1	2.29	0.53	14.08
15			323.15	0.7792	1121.4	1147.9	1102.8	1264.6	2.37	1.66	12.77
16	tert-Butyl alcohol	31	298.15	0.7810	1123.2	1158.9	1134.8	1251.1	3.18	1.03	11.39
17	n-Butylamine	32	303.15	0.7279	1232.0	1146.5	1098.7	1240.6	6.94	10.82	0.70
18	sec-Butyl amine	32	303.15	0.7136	1154.0	1108.4	992.7	1112.4	3.95	13.97	3.60
19	Butric acid	33	303.15	0.9463	1188.9	1254.5	1439.1	1620.9	5.51	21.05	36.34
20	m-Cresol	34	308.15	1.0200	1452.0	1169.6	1166.4	1257.1	19.45	19.67	13.42
21	Cyclohexanol	27	303.15	0.9421	1446.1	1230.3	1357.5	1430.6	14.92	6.13	1.07
22			308.15	0.9391	1423.4	1226.4	1344.6	1417.0	13.84	5.54	0.45
23			313.15	0.9343	1406.1	1220.1	1324.1	1395.4	13.23	5.83	0.76
24			318.15	0.9302	1382.2	1214.7	1306.7	1377.1	12.12	5.46	0.37
25	Diethyl amine	35	303.15	0.6954	1090.0	1144.8	1093.6	1202.2	5.02	0.33	10.29
26	1-Dodecanol	36	313.15	0.8218	1360.9	1266.7	1481.6	1193.2	6.92	8.87	12.33
27	Ethyl acetate	28	303.15	0.8884	1128.0	1153.6	1119.1	1150.5	2.27	0.79	1.99
28	1- Heptanol	37	303.15	0.8157	1310.0	1221.4	1328.5	1308.1	6.76	1.41	0.15
29	1-Hexanol	37	303.15	0.8120	1288.0	1211.2	1295.3	1335.1	5.96	0.56	3.66
30	Methyl acetate	38	303.15	0.9260	1137.0	1140.0	1080.0	1191.8	0.26	5.01	4.82
31	Monoethanolamine	39	303.15	1.0044	1737.9	1289.1	1561.8	2088.9	25.82	10.14	20.20
32			308.15	1.0018	1715.0	1285.8	1549.7	2072.7	25.03	9.64	20.86
33			313.15	0.9989	1707.6	1282.1	1536.2	2054.8	24.92	10.04	20.33
34			318.15	0.9936	1680.0	1275.3	1511.9	2022.2	24.09	10.00	20.37
35			323.15	0.9903	1664.1	1271.0	1496.9	2002.2	23.62	10.05	20.31
36			328.15	0.9871	1630.0	1266.9	1482.4	1982.8	22.27	9.05	21.64
37	1-Octanol	40	303.15	0.8219	1332.0	1236.9	1379.7	1308.3	7.14	3.58	1.78
38	2-Octanol	40	303.15	0.7955	1291.0	1207.0	1281.9	1196.1	6.51	0.70	7.35

39	1-Pentanol	41	303.15	0.8076	1260.0	1194.7	1243.0	1352.1	5.18	1.35	7.31
40	1-propanol	42	123.15	0.9440	2349.0	1372.9	1886.4	2378.3	41.55	19.69	1.25
41			128.15	0.9400	2225.0	1367.1	1862.6	2348.2	38.56	16.29	5.54
42			133.15	0.9360	2118.0	1361.3	1838.9	2318.4	35.73	13.18	9.46
43			138.15	0.9320	2031.0	1355.4	1815.4	2288.8	33.26	10.62	12.69
44			143.15	0.9270	1952.0	1348.2	1786.3	2252.1	30.93	8.49	15.37
45			148.15	0.9230	1887.0	1342.4	1763.3	2223.1	28.86	6.55	17.81
46			153.15	0.9190	1838.0	1336.5	1740.5	2194.3	27.28	5.31	19.39
47			158.15	0.9150	1797.0	1330.7	1717.9	2165.8	25.95	4.40	20.52
48			163.15	0.9110	1764.0	1324.9	1695.4	2137.5	24.89	3.89	21.17
49			173.15	0.9020	1713.0	1311.8	1645.7	2074.8	23.42	3.93	21.12
50			183.15	0.8940	1663.0	1300.2	1602.3	2020.1	21.82	3.65	21.47
51			213.15	0.8690	1533.0	1263.8	1471.6	1855.3	17.56	4.01	21.02
52			243.15	0.8440	1407.0	1227.5	1348.2	1699.7	12.76	4.18	20.81
53			275.15	0.8170	1287.0	1188.2	1222.9	1541.8	7.68	4.98	19.80
54	2- propanol	43	303.15	0.7621	1112.0	1116.0	1013.2	1243.1	0.36	8.89	11.79
55			313.15	0.7553	1084.0	1106.0	986.3	1210.1	2.03	9.02	11.63
56			323.15	0.7443	1038.0	1089.9	943.8	1158.0	5.00	9.07	11.56
57	Propionic acid	44	308.15	0.9671	1109.0	1201.0	1263.0	1531.5	8.30	13.89	38.10
58	n-Propyl acetate	28	303.15	0.8762	1150.0	1183.8	1209.5	1183.4	2.94	5.17	2.91
59	Propylene glycol	27	303.15	1.0295	1494.2	1282.5	1538.0	1859.5	14.17	2.93	24.45
60			308.15	1.0259	1478.5	1278.1	1521.9	1840.0	13.56	2.93	24.45
61			313.15	1.0222	1467.9	1273.5	1505.5	1820.2	13.25	2.56	24.00
62			318.15	1.0179	1451.0	1268.1	1486.6	1797.3	12.61	2.45	23.87
63	Pyridine	31	293.15	0.9778	1417.8	1255.9	1444.2	1705.7	11.42	1.86	20.31
	Average absolute percentage deviation for 63 data points								12.97	5.81	13.19

This also gives the predicted ultrasonic velocities as well as absolute average deviations in the predicted velocities. The pure organic liquid properties required for the calculation are given in table 2.

Table - 2 Physical properties of Pure Liquids

S.No	Liquid	Molecular weight	Boiling Point K	Critical Temp K	Critical Volume $Cm^3/gmol$
1	iso- Amyl alcohol	88.150	404.4	579.5	329
2	Benzyl alcohol	108.140	478.6	677.0	334
3	n-Butyl acetate	116.160	399.2	579.0	400
4	n-Butyl alcohol	74.123	390.9	562.9	274
5	iso- Butyl alcohol	74.123	381.0	547.7	273
6	tert-Butyl alcohol	74.123	355.6	506.2	275
7	n-Butylamine	73.139	350.6	524.0	288
8	sec-Butyl amine	73.139	340.6	516.0	284
9	Butric acid	88.107	436.4	628.0	292
10	m-Cresol	108.140	475.4	705.8	310
11	Cyclohexanol	100.161	434.3	625.0	327
12	Diethyl amine	73.139	328.6	496.6	301
13	1-Dodecanol	186.339	533.1	679.0	718
14	Ethyl acetate	88.107	350.3	523.2	286
15	1- Heptanol	116.204	449.5	633.0	435
16	1-Hexanol	102.177	430.2	610.0	381
17	Methyl acetate	74.080	330.1	506.8	228
18	Monoethanolamine	61.084	443.5	614.0	196
19	1-Octanol	130.231	468.4	658.0	490
20	2-Octanol	130.231	452.9	637.0	494
21	1-Pentanol	88.150	411.0	586.0	326
22	1-propanol	60.096	370.4	536.7	218.5
23	2- propanol	60.096	355.4	508.3	220
24	Propionic acid	74.080	414.0	612.0	230
25	n-Propyl acetate	102.134	374.8	549.4	345
26	Propylene glycol	76.096	460.5	625.0	237
27	Pyridine	79.102	620.0	388.5	254

Important Note:
The Data taken from "Reid, R.C., Prausnitz, J.M., and Sherwood, T.M., The properties of gases and liquids 3rd Edition McGraw-Hill Company,Newyork,1977".

The results in table 1 indicate that Model 2 is good in predicting the ultrasonic velocity in the associated liquids with an absolute average deviation of 5.81%.The predicted ultrasonic velocity in pure liquids by using Model 1 and 3 gives 10.7% and 9.8% of absolute average deviation respectively.

CONCLUSION

This paper presents new expressions for ultrasonic velocity calculation by theoretical method. In the overall performance Model 2 is superior to Models 1 and 3 which give comparable accuracy in the prediction of ultrasonic velocity in pure liquids. These expressions may also represent an accurate and generalized expression to predict ultrasonic velocity of pure liquids of industrial interest.

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