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Theoretical Models of Ultrasonic Velocities in binary liquid mixtures

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Abstract

Ultrasonic velocity is one of the important tools for understanding molecular interaction of binary liquid mixtures. Hence, various theoretical models were devised for calculating ultrasonic velocity. In this work, Impedance relation, Nomoto's Relation, Rao's specific velocity relation, Van Dael-Vangeel Ideal mixture relation, and Junjie's relation are considered and the calculated velocities are compared with the experimental values. The theory which gives the closest agreement is analysed and justified. The binary mixtures of octan-1-ol and methyl at 4 different temperaturesover a range of concentrations are considered. A secondary study is also considered to confirm the inferences.

Keywords: Nomoto's, Junjie's, octan-1-ol, MMA, dipole.

Introduction

Ultrasonic velocity (USV) is one of the ways to derive information about physical behaviour of liquid mixtures and there exist numerous models of calculating it theoretically from given or observed factors. Studies in USVcan help us in determining interactions between the studied substances on a molecular level. Based on this, theories have been put forth to explain the results obtained. The mathematical models used in the following study include but are not limited to: the Impedance relation, Nomoto's Relation, Rao's specific velocity relation, Van Dael-Vangeel Ideal mixture relation, and Junjie's relation. The experimental values from the paper published by Sridevi Gutta involving octan-1-ol and methyl benzoate will be used for analysis[1]. The theoretical values of USV are compared with the experimental values to calculate the error percentage and conclude which model used is the most accurate for calculating USV in binary mixtures of liquids. Molecular interactions in binary mixtures are studied based on the deviation in the values of U^2_{exp}/U^2_{IMR}. The analysis and justification for the model in the closest agreement with experimental values is offered.The chemical reagents used are 1-octanol and methyl benzoate.

The USV and densities for the individual substances are given in table-1 for 4 different temperatures. These have been gathered from various literature sources. The USV for 10 mole fractions of binary mixtures are recorded in table-2 as reported in the liturature[1,2].

Table-1
Density and ultrasonic sound speeds values of pure liquids across the temperature range

Component	303.15 K		308.15 K	
	Density, ρ (kg/m3)	Velocity, U (m/s)	Density, ρ (kg/m3)	Velocity, U (m/s)
Methyl Benzoate	1087.5	1404	1085.9	1376.84
1-Octanol	803.3	1365	801.6	1326.31
Component	**313.15 K**		**318.15 K**	
	Density, ρ (kg/m3)	**Velocity, U (m/s)**	**Density, ρ (kg/m3)**	**Velocity, U (m/s)**
Methyl Benzoate	1081.4	1367.36	1083.8	1348.42
1-Octanol	800	1303.33	798.1	1291.57

Table-2
Experimental values of ultrasonic sounds across the range of temperatures and concentrations

303.15 K		308.15 K		313.15 K		318.15 K	
X_1	U_{exp}	X_1	U_{exp}	X_1	U_{exp}	X_1	U_{exp}
0	1365	0	1326.32	0	1303.34	0	1291.58
0.1259	1370.53	0.1259	1329.48	0.1259	1306.67	0.1259	1301.06
0.2447	1371.82	0.2447	1333.34	0.2447	1306.67	0.2447	1302.36
0.358	1376.83	0.358	1343.34	0.358	1320.1	0.358	1310.53
0.4635	1380.1	0.4635	1348.44	0.4635	1332.64	0.4635	1312.95
0.5642	1383.5	0.5642	1351.74	0.5642	1335.79	0.5642	1314.87
0.6601	1387.06	0.6601	1354.64	0.6601	1335.79	0.6601	1320.1
0.7513	1390.2	0.7513	1357.88	0.7513	1338.95	0.7513	1323.1
0.8381	1396.67	0.8381	1369.44	0.8381	1346.67	0.8381	1326.1
0.920	1400.1	0.920	1373.69	0.920	1354.74	0.920	1330.1
1	1404	1	1376.85	1	1367.37	1	1348.43

In the first study scenario referred to here, methyl benzoate is "1" and octan-1-ol is "2"."

In the secondary study considered to confirm our findings, the substances used are methyl methacrylate and 3 aryl esters/alcohols - 2-methoxy ethanol, 2-ethoxy ethanol, 2-butoxy ethanol. This study is conducted at a fixed temperature with gradually increasing mole fractions[3].

Methodology

Nomoto's Relation: This relation was set up by O. Nomoto[4] in 1958. The relation is as follows:

$$U = \left(\frac{\Sigma x_i R_i}{\Sigma x_i V_i}\right)^3 => \quad (1)$$

Where: $R = \left(\frac{M_i}{\rho_i}\right)(U_i)^{\frac{1}{3}}$; and $V_i = M_i/\rho_i$, Where, M = molar mass; ρ = density; V = molar volume; x = molar fraction

Impedance relation: The impedance relation[5] is:

$$\frac{\sum x_i Z_i}{\sum x_i \rho_i} => \quad (2)$$

Where $Z = \rho U$ Z = acoustic impedance

Van Dael Vangeel Relation: The Van dael Vangeel Ideal Mixing relation (IMR)[6,7] is given by:

$$U = \left[\frac{1}{x_1 M_1 + x_2 M_2}\right]^{\frac{1}{2}} \left[\frac{x_1}{U_2^2 M_1} + \frac{x_2}{U_2^2 M_2}\right]^{-\frac{1}{2}} => \quad (3)$$

Rao's Specific Sound Velocity:

$$U = \left(\sum x_i r_i \rho_i\right)^3 => \quad (3)$$

Where, $r_i = \frac{U_i^{1/3}}{\rho_i}$ r = Rao's specific sound velocity[8]

Junjie's Relation: Junjie's relation[9,10] is given by:

$$U = \frac{x_1 V_1 + x_2 V_2}{(x_1 M_1 + x_2 M_2)^{\frac{1}{2}}} \left[\frac{x_1 M_1}{U_1^2 \rho_1} + \frac{x_2 M_2}{U_2^2 \rho_2}\right]^{-\frac{1}{2}} => \quad (5)$$

Calculations: The calculations were performed using MATLAB R2011a and the results were imported and plotted in graphs using Microsoft Excel. Experimental observations were taken from literature sources and compared with the calculated values in the form of percentage errors and chi square values[11,12]. Observations along with the experimental values were calculated and tabulated. In the following section we will see the graphical representation of percentage error and chi square relation for each equation.

Results and Discussion

Percentage error: This kind of test has been carried out in binary mixtures before however it has been carried out in a mixture of fatty primary alcohol and ester only in some cases. The structure of Methyl Benzoate, an ester, is as follows:

When the two liquid substances are mixed and forma binary mixture, various intermolecular forces such as hydrogen bonding, charge transfer, dispersive forces, and dipole-induced dipole interactions, come into play. This causes a change in volume in the mixture and thus the observed values deviate from the calculated values[13]. This can be explained by observing the structures of the molecules involved and their interactions. The structure allows oxygen atoms to cause dipole moments towards themselves and this gives the molecule a net dipole of approximately 6.2[14]. This induces a dipole in the non-polar octan-1-ol and thus causes a closer bond than simple Vander Vaal's forces. This changes the volume from the ideal condition and thus causes the changes in calculated results from all the theoretical models. However since the deviation observed was smallest in this model for the concentration of 0.3 to 0.4 (approximately at 0.357), it indicates that the denser liquid 1 (methyl benzoate) is in the optimum concentration with minimum molecular interaction to affect the molar volume of that species in such a way that it reduces the ultrasonic velocity and gives a value closer to the observed one.

Similarly in the impedance relation, the change in volume and the non-additivity of the acoustic impedance factor cause the deviations from observed values.

In the case of Rao's specific velocity the error occurs due to non-additivity of the specific velocity factor and fact that mole ratios cannot be the only deciding factors in the final equation.

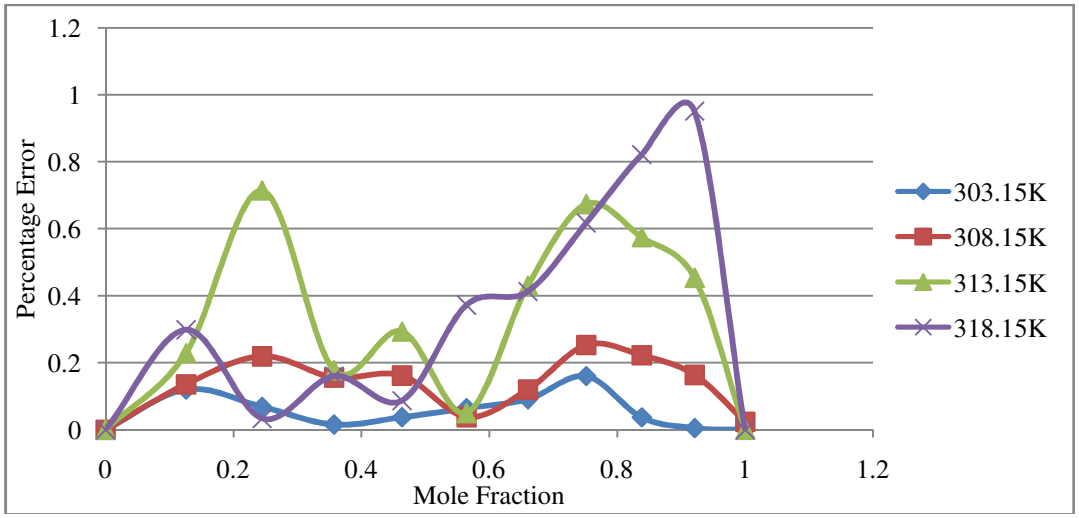

Figure-1
Nomoto's Relation

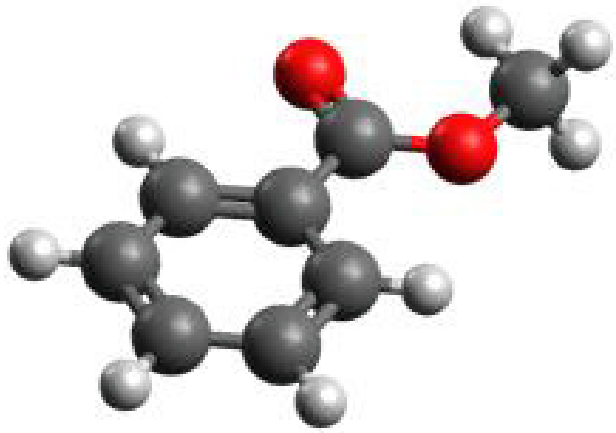

Figure-2
3-D structure of Methyl Benzoate Molecule (Red=oxygen)

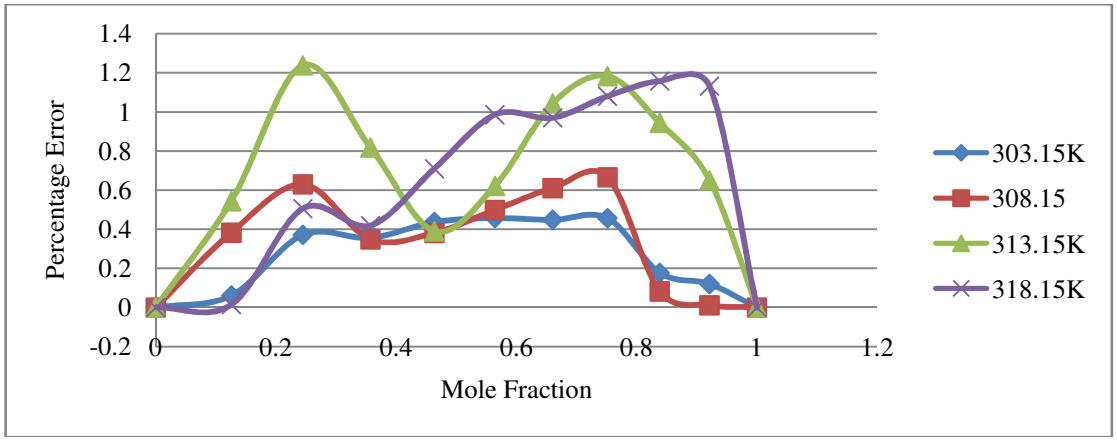

Figure-3
Acoustic Impedance Relation

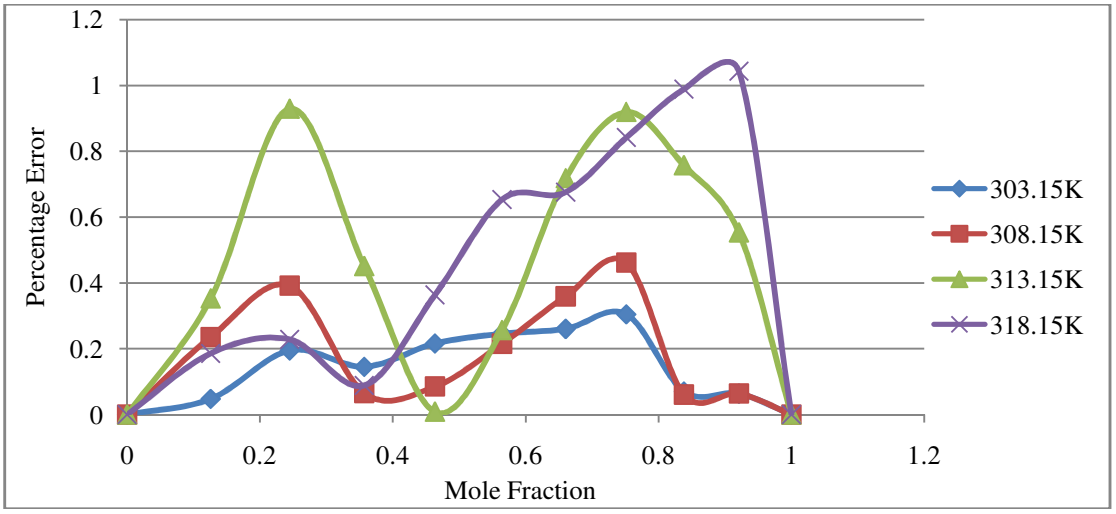

Figure-4
Rao's Specific Sound Velocity

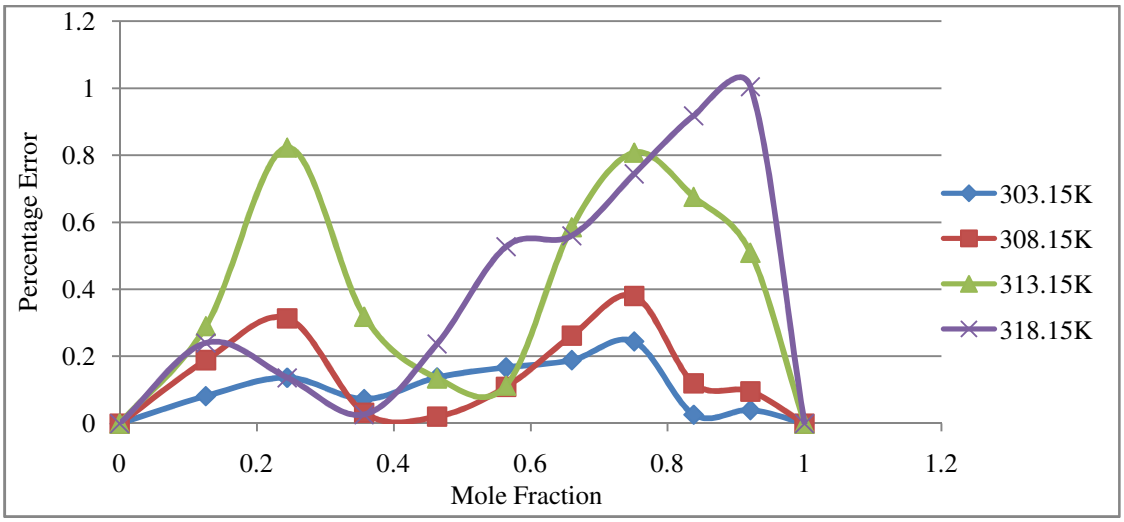

Figure-5
Ideal Mixture Relation

In the Van Dael-Vangeel IMR method, deviations from experimental values of the theoretical values may be because of the compressibility of the component liquids in the present mixture. This means that isothermal compressibility at each of the temperatures is changed when minor changes in pressure cause minor changes in volume which affect the density and hence the molar volume. This can be avoided by using components where the molecular sizes are comparable, and the polar interactions are kept to a minimum.

Chi square relations: When we compare the chi square values for all mathematical models considered, we observe that Nomoto's relation shows the least amount of deviation, followed by Vangeel IMR and then impedance and Rao's relation, and lastly Junjie's relation. This gives the accuracy of each theoretical model over all the range of data points combined.

Table-3
Chi square calculations for Nomoto's Relation

Nomoto's Relation				
X1	**303.15K**	**308.15K**	**313.15K**	**318.15K**
0	9.11E-15	6.92E-15	6.78E-17	3.94E-14
0.1258	0.001995	0.002441	0.006829	0.011624
0.2446	0.000648	0.006375	0.066147	0.000144
0.357	3.30E-05	0.003259	0.004177	0.003363
0.4634	0.000192	0.003531	0.011477	0.000984
0.5643	0.000572	0.000191	0.00033	0.018116
0.6602	0.001152	0.001934	0.024642	0.022372
0.7514	0.003559	0.008641	0.060369	0.050026
0.8382	0.000192	0.006763	0.044313	0.088744
0.921	3.33E-06	0.00367	0.027751	0.11913
1	2.12E-12	7.72E-05	3.44E-17	9.82E-14
	0.008346	0.036882	0.246036	0.314503

Table-4
Chi square calculations for Van Dael-Vangeel Ideal Mixing Relation

Vangeel Ideal Mixing Relation				
X1	**303.15K**	**308.15K**	**313.15K**	**318.15K**
0	3.79E-29	3.90E-29	0	0
0.1258	0.00092	0.004747	0.011016	0.007514
0.2446	0.002568	0.013075	0.087835	0.002416
0.357	0.000732	0.00014	0.013377	9.40E-05
0.4634	0.0026	5.94E-05	0.00243	0.007383
0.5643	0.003868	0.001616	0.001711	0.036389
0.6602	0.004942	0.009283	0.045535	0.041175
0.7514	0.008304	0.019557	0.086717	0.072796
0.8382	9.80E-05	0.001972	0.061155	0.110659
0.921	0.000226	0.001263	0.034996	0.132849
1	0	3.75E-29	0	3.83E-29
	0.024258	0.051714	0.344771	0.411274

To further confirm the methods of analysis used, another similar experimental set up was considered and the theoretical models were applied for it in the same way as presented above. [15]The liquids used were similar but differed in the fact that there was no aromatic compound used. The mixtures were of methylmethacrylate with 3 aryl esters/alcohols - 2-methoxy ethanol, 2-ethoxy ethanol, 2-butoxy ethanol. The temperature was kept constant at 303.15K and the molar concentrations of all 3 mixtures were varied from 0.1 to 0.9 in increments of 0.1. Instead of Rao's specific velocity and the impedance relation, free length theory and collision theory were considered[16, 17].

The following is a series of tables of the experimental values observed for varying concentration of methyl methacrylate (X1), and its comparison to the calculated value using the various theories. The percentage error is also specified. These are followed by the plots of percentage error vs. mole fraction. This graphical representation gives us a good idea about the accuracy of each theory.

Table-5
Chi square calculations for Impedance relation

Impedance Relation				
X1	**303.15K**	**308.15K**	**313.15K**	**318.15K**
0	0	0	0	0
0.1258	0.000514	0.019437	0.038546	2.68E-05
0.2446	0.018855	0.052752	0.199946	0.033275
0.357	0.017404	0.01624	0.088069	0.022979
0.4634	0.026264	0.019539	0.02019	0.066084
0.5643	0.028829	0.033561	0.051604	0.127606
0.6602	0.027777	0.050457	0.145121	0.124026
0.7514	0.028924	0.060069	0.18715	0.154194
0.8382	0.004379	0.000929	0.119751	0.177571
0.921	0.002007	1.66E-05	0.057284	0.170131
1	0	0	0	0
	0.154953	**0.253001**	**0.907661**	**0.875893**

Table-6
Chi square calculations for Junjie's relation

X1	303.15K	308.15K	313.15K	318.15K
0	4.63E-09	1.39E-10	5.10E-09	2.22E-09
0.1258	0.050925	0.019215	0.013101	0.091973
0.2446	0.088281	0.065483	0.009019	0.113812
0.357	0.185888	0.25114	0.162236	0.271231
0.4634	0.225362	0.32518	0.419517	0.251811
0.5643	0.23833	0.301962	0.344136	0.18133
0.6602	0.212789	0.2246	0.155215	0.155747
0.7514	0.142294	0.132058	0.058645	0.066679
0.8382	0.122714	0.1873	0.027835	0.005502
0.921	0.035882	0.065763	0.002416	0.017617
1	4.38E-11	1.18E-10	1.71E-10	1.66E-10
	1.302465	1.5727	1.192119	1.155703

Table-7
Chi square calculations for Rao's Specific velocity relation

Rao's Specific Velocity Relation				
X1	303.15K	308.15K	313.15K	318.15K
0	1.51E-28	3.51E-28	3.57E-28	0
0.1258	0.000312	0.00734	0.016226	0.004502
0.2446	0.005194	0.020383	0.111805	0.00678
0.357	0.002898	0.000569	0.026735	0.001023
0.4634	0.006428	0.000978	1.03E-05	0.017277
0.5643	0.008323	0.006248	0.008787	0.055751
0.6602	0.0094	0.017434	0.068399	0.059861
0.7514	0.012871	0.028823	0.112158	0.092926
0.8382	0.000687	0.000505	0.07669	0.128363
0.921	0.000568	0.000561	0.04126	0.143138
1	1.47E-28	1.84E-27	2.42E-27	1.38E-27
	0.046682	0.082842	0.462069	0.50962

In our secondary set up, observing the percentage error plots tells us that the free length theory with a maximum of over 3.5 % deviation is the least accurate method for binary mixtures where dipole-dipole interactions are present[18]. In the case of these mixtures, the methyl methacrylate and other alcohols all have strong dipoles which give rise to dipole-dipole interactions. This causes changes in volumes which are not a result of pressure changes. This causes the deviations in adiabatic compressibility and therefore a change in the value of intermolecular free length.

If we consider the collision factor theory the "actual volume" factor in the equation again does not consider the very strong hydrogen bonding and dipole-dipole interactions in the compounds and thus it gives a deviation. This would not have been the case in case of a mixture with slightly weaker interactions such as dipole-induced dipole and weak Van Der Waal's forces.

Thus from the graph we see that our previous conclusion of Nomoto's theory being the most accurate one is supported by our secondary observations as well. Thus in both cases, despite there being a strong presence of dipole-dipole interactions and even hydrogen bonding in the second case, Nomoto's theory gives the least amount of error.

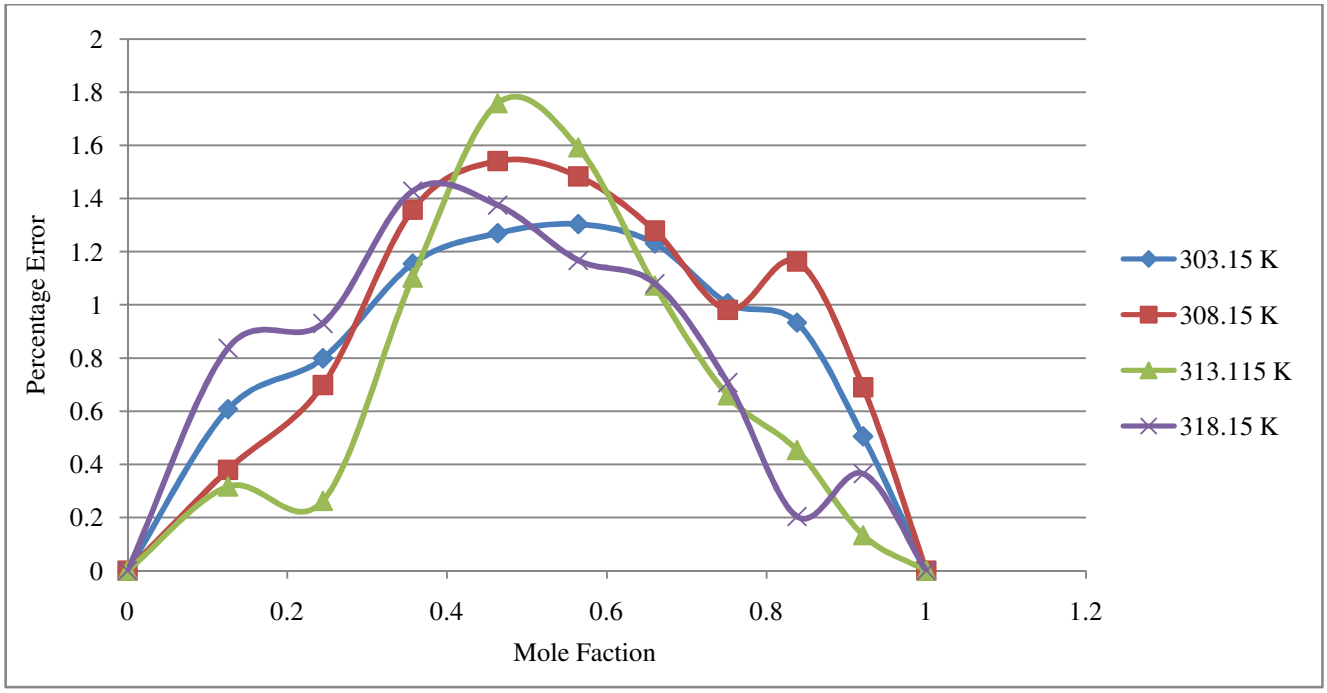

Figure-6
Junjie's Relation

Table-8
For 2-methoxy ethanol

X1	U_{exp} (m/s)	U_{FLT}	$U_{Nomoto's}$	U_{CFT}	U_{IMR}	$U_{Junjie's}$	$PE_{Nomoto's}$	PE_{FLT}	PE_{CFT}	PE_{IMR}	$PE_{Junjie's}$
0.1	1421	1416	1418.01	1418	1413	1418	0.21	0.34	0.23	0.62	0.23
0.2	1408	1388	1402.23	1400	1402	1399	0.41	1.43	0.56	0.43	0.64
0.3	1246	1210	1240.64	1234	1246	1236	0.43	2.89	0.94	0.79	0.78
0.4	1245	1205	1238.27	1229	1234	1229	0.54	3.21	1.32	0.91	1.31
0.5	1235	1193	1228.94	1216	1220	1214	0.49	3.39	1.56	1.24	1.67
0.6	1069	1024	1065.58	1055	1055	1083	0.32	4.23	1.32	1.31	-1.32
0.7	1008	975	1005.89	999	998	1018	0.21	3.24	0.89	0.98	-1.03
0.8	930	911	928.23	926	923	938	0.19	2.04	0.46	0.76	-0.86
0.9	920	916	919.12	917	917	923.8	0.11	0.42	0.38	0.38	-0.41
AVG PE							0.32	2.35	0.85	0.82	0.92

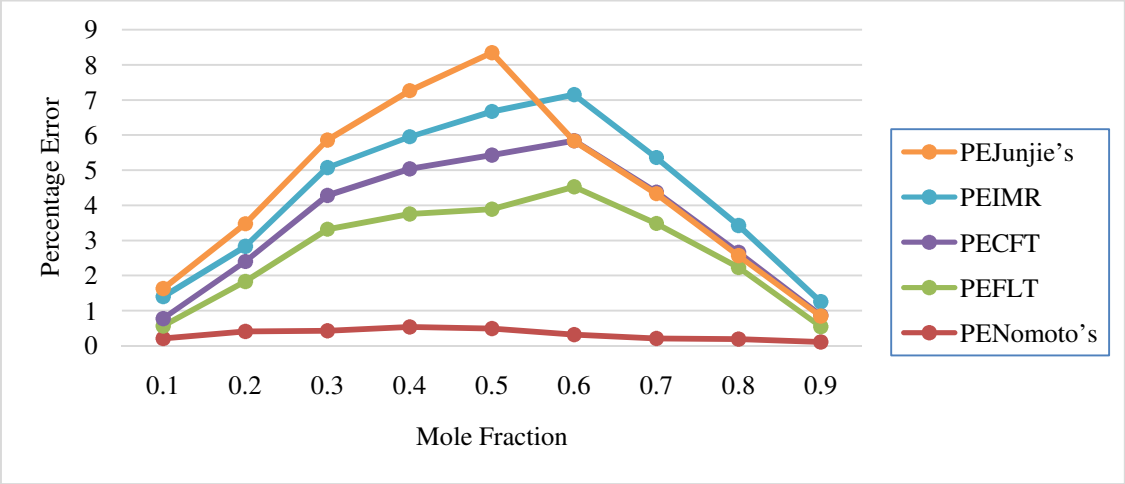

Figure-7
For 2-methoxy ethanol

Table-9
For 2-ethoxy ethanol

X1	U_{exp}(m/s)	U_{FLT}	$U_{Nomoto's}$	U_{CFT}	U_{IMR}	$U_{Junjie's}$	$PE_{Nomoto's}$	PE_{FLT}	PE_{CFT}	PE_{IMR}	$PE_{Junjie's}$
0.1	1638	1631	1632.26	1634	1631	1634.7	0.35	0.4	0.3	0.4	0.2
0.2	1500	1458	1495.37	1491	1488	1492.5	0.31	2.8	0.6	0.8	0.5
0.3	1460	1422	1451.53	1450	1440	1448.3	0.58	2.6	0.7	1.4	0.8
0.4	1360	1315	1351.56	1348	1334	1336.9	0.62	3.3	0.9	1.9	1.7
0.5	1232	1188	1226.33	1221	1202	1208.6	0.46	3.6	0.8	2.4	1.9
0.6	1080	1043	1075.47	1070	1051	1060.6	0.42	3.4	0.9	2.7	1.8
0.7	1000	971	995.63	992	977	985.2	0.44	2.9	0.7	2.3	1.4
0.8	920	894	917.056	914	912	912.66	0.32	2.8	0.5	0.9	0.8
0.9	600	598	598.44	597	598	597.63	0.26	0.3	0.4	0.4	0.4
AVG PE							0.41	2.45	0.64	1.46	1.05

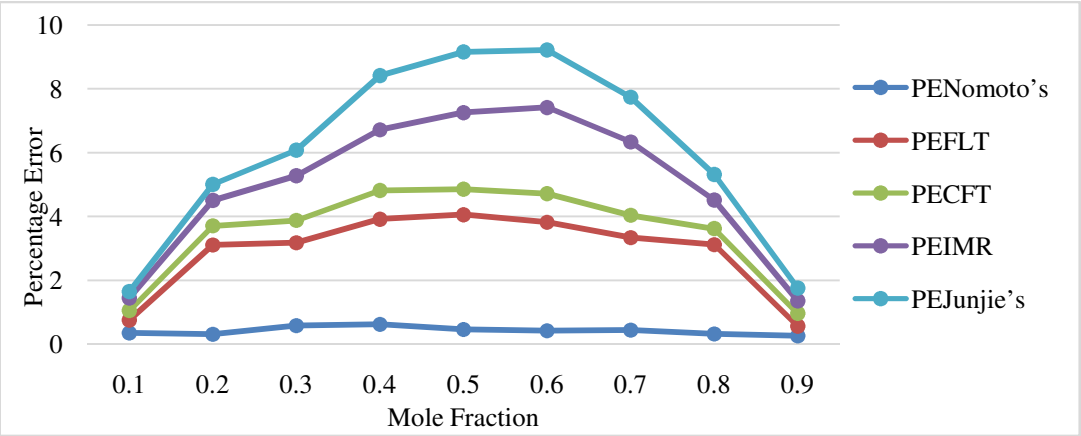

Figure-8
For 2-ethoxy ethanol

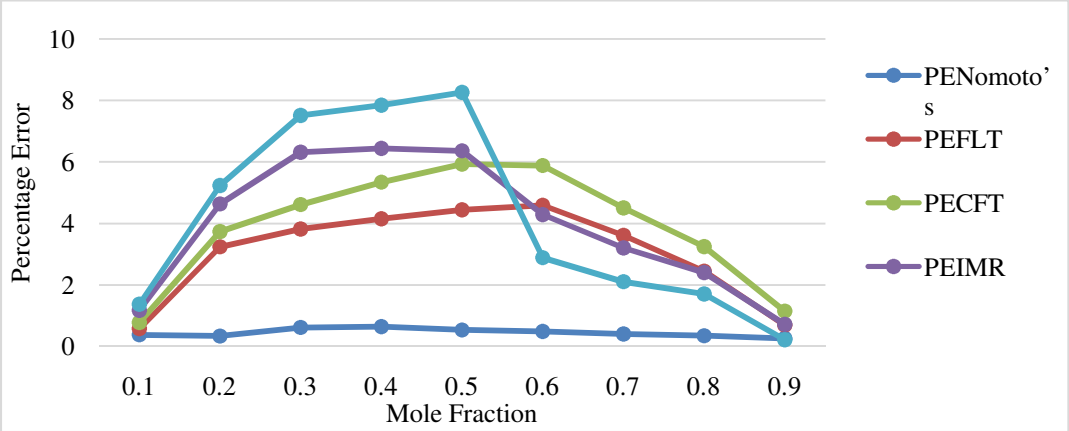

Figure-9
For 2-butoxy ethanol

Table-10
For 2-butoxy ethanol

X1	U_{exp}(m/s)	U_{FLT}	$U_{Nomoto's}$	U_{CFT}	U_{IMR}	$U_{Junjie's}$	$PE_{Nomoto's}$	PE_{FLT}	PE_{CFT}	PE_{IMR}	$PE_{Junjie's}$
0.1	2240	2236	2231.49	2236	2231	2235.5	0.38	0.2	0.2	0.4	0.2
0.2	1530	1483	1524.8	1522	1516	1520.9	0.34	2.9	0.5	0.9	0.6
0.3	1498	1450	1488.71	1486	1473	1480.1	0.62	3.2	0.8	1.7	1.2
0.4	1474	1422	1464.42	1456	1458	1453.4	0.65	3.5	1.2	1.1	1.4
0.5	1440	1384	1432.22	1419	1434	1412.9	0.54	3.9	1.5	0.43	1.9
0.6	1418	1360	1411.05	1400	1441	1437.9	0.49	4.1	1.3	-1.6	-1.4
0.7	1230	1212	1224.96	1219	1246	1243.6	0.41	3.2	0.9	-1.3	-1.1
0.8	990	969	985.535	982	998	997.01	0.35	2.1	0.8	-0.84	-0.7
0.9	680	677	675.784	678	683	683.52	0.26	0.43	0.46	-0.43	-0.5
AVG PE							0.44	2.61	0.85	0.96	1

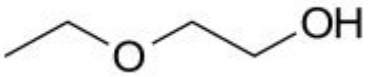

Figure-10
2 Ethoxy ethanol

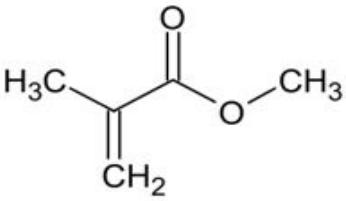

Figure-11
Methyl Methacrylate

Conclusion

Thus we can conclude that Nomoto's relation is the closest to theoretical values, followed by Vangeel IMR and impedance relation, and then Rao's specific velocity relation and finally Junjies's relation. Further improvements to accuracy can be made through the establishing of a relationship between dipole-induced dipole interactions and changes in volume, and appending these factors into the existing theories.

References

1. Sridevi G and Fakruddin Sk, Experimental and Theoretical Studies of Ultrasonic Velocity in Binary Liquid Mixtures of Methyl Benzoate at Different Temperatures, *Journal of Chemical and Pharmaceutical*

Research, **4(8)**, 3792-3796 **(2012)**

2. Gutta Sridevi, Ultrasonic Study of Acoustical Parameters of Binary Liquid Mixtures of Methyl Benzoate with 1-Octanol at 303.15K, 308.15K, 313.15K and 318.15K, *Research Journal of Chemical Sciences,* **3(3)**, 14-19, **(2013)**

3. Shaik Babu S.V., Kumara Shastry, Ha SieTiong and Sreehari Sastry S., Experimental and Theoretical Studies of Ultrasonic Velocity in Binary Liquid Mixtures of Ethyl benzoate, *E-Journal of Chemistry*, **9(4)**, 2309-2314 **(2012)**

4. Nomoto O, *J Phys Soc Jpn*.,**13**, 1528 **(1958)**

5. Shanmuga Priya C., Nitya S., Velraj G. and Kannappan A.N., Molecular interaction studies in liquid mixture using ultrasonic technique, *International Journal of Advanced Science and Technology*, **18**, 59-73 **(2010)**

6. Zareena Begum P.B., Sandhya Sri and Rambabu C., Theoretical Evaluation of Ultrasonic Velocities in Binary Liquid Mixtures of Anisaldehyde with Some Alcoxyethanols at Different Temperatures, *ISRN Physical Chemistry,* vol. 2012, Article ID 943429, 12 pages, **(2012)**

7. Van Dael W and Vangeel E, Proc IntConf on calorimetry and thermodynamics, Warasa, **1955**, 555

8. Durga Bhavani M., Ratnakar A. and Kavitha Ch., *International Letters of Chemistry, Physics and Astronomy,* **5,** 1-6 **(2013)**

9. GV Rama Rao, PB Sandhya Sri, A Vishwanatha Sarma and C Rambabu, *Indian Journal of Pure and Applied Physics,* **45,** 135-142 (**2007**)

10. Junjie Z, *J China UnivSci Tech*., **14,** 298 **(1984)**

11. Praveen Babu G., Pavan Kumar B. and Nagarjun K. Samatha, *International Letters of Chemistry, Physics and Astronomy,* **11(1)** 9-17 **(2014)**

12. Uvarani R. and Punitha S., Theoretical Prediction of Ultrasonic Velocity in Organic Liquid Mixtures, *E-Journal of Chemistry*, **6(S1),** S235-S238 **(2009)**

13. Pandey JD, Singh AK and Ranjan Dey, Novel approach for prediction of ultrasonic velocity in quaternary liquid mixtures, *Pramana Journal of Physics, Indian Academy of Sciences,* **64(1),** 135-139 **(2005)**

14. http://www.vias.org/genchem/dipole_moment_table.html **(2015)**

15. Bedare G.R., Bhandakkarand V.D. and Suryavanshi B.M., Ultrasonic Study of Methylmethacrylate in 1, 4-dioxane at 298 K and 2 MHz Frequency, *International Journal of Research in Pure and Applied Physics*, **3(3),** 20-22 **(2013)**

16. Pandey J.D., Vinay Sanguri, Yadav M.K. and Aruna Singh, Intermolecular free length and free volume of pure liquids at varying temperatures and pressures, *Indian Journal of Chemistry,* **47A**, 1020-1025, **(2008)**

17. Schaaffs W, *Acustica,* **33,** 27 (**1975**)

18. Al Kandary JA, AL Jimaz AS, Abdul Haq M and Abdul Latif, *J ChemEng Data,* **51,** 2074, (**2006**)