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## Theoretical Evaluation of Ultrasonic Velocity in Organic Liquid Mixtures

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**Abstract:** Theoretical values of ultrasonic velocity in four ternary liquid mixtures of 1-propanol, 1-butanol, 1-pentanol and 1-hexanol with TEA in n-hexane for different proportions have been evaluated using Nomoto's Relation, Ideal Mixture Relation, Free Length Theory and Impedence Dependence Relation. Theoretical values are compared with experimental values and the Chi-square test for goodness of fit is applied to check the validity of the theories.

**Key words:** Ultrasonic velocity, Chi-square, liquids, molecular interaction

### INTRODUCTION

Measurement of ultrasonic study gives information about physico-chemical behaviour of solutions and liquid mixtures and molecular interactions of multicomponent liquid mixtures. In this context Ramaswamy *et al.* (1980) carried out ultrasonic investigation on some binary and ternary liquid mixtures and correlated the experimental findings of ultrasonic velocity with the theoretical relations suggested by Nomoto (1958) and Van Deal and Vangeel (1969) and interpreted the results in terms of molecular interactions. Kannappan *et al.* (2003) have also computed the ultrasonic velocity of liquid mixtures using both the relations and discussed the applicability of the same. The Free Length Theory (FLT) based upon Jacobson (1952) concept of intermolecular free length has been successfully applied by many workers to evaluate ultrasonic velocities in liquids. All the four theories have been successfully applied by Kannappan and Rajendran (1990). Palaniappan and Ramesh (2001) have calculated the sound velocity and interpreted the results in terms of molecular interactions. This investigation presents the evaluation of ultrasonic velocity using Nomoto's relation, ideal mixtures relation, free length theory and impedence dependance relation for propanol, butanol, pentanol and hexanol with TEA in n-hexane and comparison with experimentally observed values.

### THEORY

**Nomoto's Relation (NR):** The empirical formula for sound velocity in liquid mixtures given by Nomoto can be written as:

$$U_{NR} = \left[ \frac{X_1 R_1 + X_2 R_2 + X_3 R_3}{X_1 V_1 + X_2 V_2 + X_3 V_3} \right]^3 \quad (1)$$

where,  $X_1$ ,  $X_2$  and  $X_3$  are the mole fractions of pure liquids,  $R$  and  $V$  represents the molar sound velocity and molar volume.

**Impedence Dependence Relation (IDR):** The product of sound velocity ( $U$ ) and the density ( $\rho$ ) of the mixture is termed as the acoustic impedance ( $z$ ) of the mixture. Hence, the sound velocity in the mixture can be predicted from the knowledge of the acoustic impedance and the density of pure components. This relation for ternary system (Kalidoss and Srinivasamoorthy, 1997) may be given as:

$$U_{IDR} = \frac{\sum_{i=1}^3 X_i z_i}{\sum_{i=1}^3 X_i \rho_i} \quad (2)$$

where, the symbols refer to their usual meaning.

**Free Length Theory (FLT):** Free Length concept in ternary liquid mixtures is introduced by Jacobson (1952) as:

$$L_{mix} = 2 \left[ \frac{V_m \cdot (X_1 V_{01} + X_2 V_{02} + X_3 V_{03})}{X_1 Y_1 + X_2 Y_2 + X_3 Y_3} \right] \quad (3)$$

where,  $V_{01}$ ,  $V_{02}$  and  $V_{03}$  represent the volume at absolute zero of the three pure components with ( $V_0 = V_{mix} U_{exp}/U_\alpha$ ),  $V_{mix}$  is the molar volume of the mixture and  $Y$  is the surface area per mole and is defined as:

$$Y = \frac{2V_{\text{mix}}}{L_{f \text{ mix}}} \left( 1 - \frac{U_{\text{exp}}}{U_{\alpha}} \right) \quad (4)$$

The degree of molecular interaction ( $\alpha$ ) is given by:

$$\alpha = \frac{U_{\text{exp}}^2}{U_{\text{imr}}^2} - 1 \quad (8)$$

Where:

$$U_{\alpha} = 1600 \text{ m sec}^{-1}$$

and also he has given the expression for  $L_f$  as:

$$L_f = \frac{K}{U_{\text{exp}} \rho_{\text{exp}}^{1/2}} \quad (5)$$

where,  $U_{\text{exp}}$  and  $\rho_{\text{exp}}$  are experimentally determined values of the sound velocity and density, respectively and  $K$  is the temperature dependent Jacobson's constant. The sound velocity in a mixture ( $U_{\text{mix}}$ ) can be calculated from the formula:

$$U_{\text{FLT}} = \frac{K}{L_{\text{mix}} \rho_{\text{exp}}^{1/2}} \quad (6)$$

**Ideal Mixture Relation (IMR):** Van Deal and Vangeel (1969) suggested the following expression for the ultrasonic velocity ( $U_{\text{imr}}$ ):

$$\frac{1}{(X_1M_1 + X_2M_2 + X_3M_3)(U_{\text{imr}}^2)} = \frac{X_1}{M_1U_1^2} + \frac{X_2}{M_2U_2^2} + \frac{X_3}{M_3U_3^2} \quad (7)$$

**Chi-square test for goodness of fit:** According to Pearson (1978) the Chi-square is given by:

$$\text{Chi-square } |\chi|^2 = \sum_{i=1}^n \left[ \frac{(O_i - E_i)^2}{E_i} \right] \quad (9)$$

where,  $O_i$  ( $i = 1, 2, 3, \dots, n$ ) is a set of observed or experimental frequencies and  $E_i$  ( $i = 1, 2, 3, \dots, n$ ) is the set of expected or theoretical frequencies.

## RESULTS AND DISCUSSION

Table 1 shows that the deviations between experimental and theoretical velocity values obtained using four methods for 1-propanol system are as: Nomoto (-1.93 to 0.48), IMR (-1.31 to 0.59), FLT (-37.8 to 2.07) and IDR (-2.95 to -1.29). The deviations observed in the remaining systems are also more or less in the same

Table 1: The experimental velocity (U), the theoretical velocity, percentage deviation and molecular interaction parameter ( $\alpha$ )

Mole fraction		Theoretical value					Percentage deviation				
$X_1$	$X_2$	U (m sec <sup>-1</sup> )	NR	IDR	FLT	IMR	NR	IDR	FLT	IMR	( $\alpha$ )
<b>1-propanol + TEA + n-hexane</b>											
0.0999	0.6000	1076.4	1097.2	1103.1	1483.3	1090.5	-1.92	-2.48	-37.80	-1.31	-0.0256
0.1999	0.5000	1081.8	1102.7	1113.7	1251.7	1094.8	-1.93	-2.95	-15.71	-1.20	-0.0235
0.2999	0.4000	1107.6	1108.9	1124.1	1149.6	1101.0	-0.12	-1.49	-3.79	0.59	0.0119
0.4000	0.3000	1114.8	1115.9	1134.2	1091.7	1109.2	-0.09	-1.74	2.07	0.50	0.0101
0.5000	0.1999	1123.2	1123.8	1144.2	1140.0	1119.8	-0.05	-1.87	-1.50	0.30	0.0060
0.6000	0.0999	1128.6	1132.7	1153.9	1184.0	1132.7	-0.36	-2.24	-4.91	-0.36	-0.0071
0.7000	0.0000	1148.6	1143.0	1163.4	1460.9	1148.1	0.48	-1.29	-27.19	0.04	0.0008
<b>1-butanol + TEA + n-hexane</b>											
0.1000	0.6000	1090.4	1100.7	1107.2	1463.7	1099.1	-0.94	-1.54	-34.24	-0.79	-0.0156
0.2000	0.4999	1107.0	1110.0	1121.8	1253.2	1110.8	-0.26	-1.33	-13.21	-0.34	-0.0067
0.2999	0.4000	1120.8	1120.0	1136.0	1120.0	1122.9	0.07	-1.36	0.07	-0.19	-0.0037
0.3999	0.2999	1132.2	1130.9	1149.9	1027.7	1135.9	0.11	-1.57	9.23	-0.33	-0.0065
0.4999	0.2000	1141.2	1142.8	1163.5	972.5	1149.5	-0.14	-1.96	14.78	-0.73	-0.0144
0.6000	0.0999	1150.2	1155.9	1176.9	940.7	1164.1	-0.49	-2.32	18.21	-1.21	-0.0237
0.6999	0.0000	1157.4	1170.3	1189.9	938.0	1179.5	-1.11	-2.81	18.96	-1.91	-0.0370
<b>1-pentanol + TEA + n-hexane</b>											
0.0999	0.6000	1100.2	1104.6	1110.9	1267.8	1102.2	-0.39	-0.97	-15.23	-0.18	-0.0035
0.1999	0.5000	1111.9	1117.7	1129.1	1199.1	1116.7	-0.52	-1.54	-7.84	-0.43	-0.0085
0.3000	0.4000	1136.2	1131.6	1146.8	1155.8	1131.6	0.40	-0.93	-1.73	0.41	0.0082
0.4000	0.2000	1147.5	1152.5	1171.2	1214.3	1280.8	-0.43	-2.07	-5.82	-11.62	-0.1973
0.5000	0.1999	1159.4	1162.0	1181.0	1122.8	1162.7	-0.22	-1.86	3.16	-0.28	-0.0056
0.6000	0.0999	1166.7	1178.6	1197.5	1146.5	1178.8	-1.02	-2.64	1.73	-1.04	-0.0204
0.7000	0.0000	1170.9	1196.3	1213.5	1200.9	1195.3	-2.17	-3.64	-2.56	-2.08	-0.0403
<b>1-hexanol + TEA + n-hexane</b>											
0.1000	0.6000	1107.7	1108.7	1114.0	1103.2	1102.1	-0.09	-0.57	0.41	0.51	0.0102
0.2000	0.5000	1118.2	1125.8	1135.2	1102.1	1116.7	-0.68	-1.52	1.44	0.14	0.0027
0.3000	0.3999	1153.5	1143.5	1155.8	1110.1	1132.0	0.86	-0.20	3.76	1.87	0.0383
0.4000	0.2999	1168.2	1161.7	1176.0	1122.8	1147.9	0.55	-0.67	3.89	1.74	0.0357
0.4999	0.1999	1182.6	1180.6	1195.6	1146.6	1164.6	0.16	-1.10	3.04	1.52	0.0311
0.6000	0.0999	1196.4	1200.1	1214.8	1191.7	1181.9	-0.31	-1.54	0.39	1.21	0.0247
0.7000	0.0000	1203.6	1220.3	1233.5	1256.5	1200.0	-1.38	-2.48	-4.40	0.30	0.0060

Table 2: The greatest percentage deviation and values of Chi-square for four theories

System	Greatest percentage deviation				Values of Chi-square			
	NR	IDR	FLT	IMR	NR	IDR	FLT	IMR
I	-0.57	-2.00	-1.00	-0.20	0.14	0.45	85.01	0.08
II	-0.39	-1.84	1.97	-0.78	0.03	0.40	35.73	0.10
III	-0.62	-1.95	-4.04	-2.17	0.10	0.51	4.97	2.07
IV	-0.12	-1.15	1.21	1.04	0.05	0.21	1.02	0.18

The Chi-square values obtained are very less than the standard Chi-square at 2% level of significance. This shows that good agreement between experimental and theoretical values of ultrasonic velocities and hence the overall validity of the theories

range. The extent of deviation in velocities may be attributed to the presumption made in the theories for non-polar-non-polar and non-polar-polar interaction between the molecules. A general survey of the Table 1 shows that  $\alpha$  is positive and small which indicates the absence of complex formation in all the systems studied. Also  $\alpha$  is maximum at 0.2999 mf with 1-propanol (0.0119), 1-butanol (-0.0037), 1-pentanol (0.0082) and 1-hexanol (0.0383). The maximum value of  $\alpha$  indicates larger deviations from ideality, which may be due to the formation of association in mixtures through hydrogen bonding.

This result is in accordance with those of Kannappan *et al.* (2003) and Jayakumar *et al.* (1996). It is inferred from the Table 2 that the percentage deviation using the relation for system IV is minimum (Chi-square is also minimum) whereas for system III it is greatest (Chi-square is also maximum).

Hexane is a nonpolar chain molecule, only Van der Waals' type interactions are present in n-hexane, while alcohols are polar and associate strongly through hydrogen bonding. In alcohols + n-hexane mixtures, the alcohol molecules associate in inert hexane medium and form clusters. Such self association factors are not taken into account in FLT or Nomoto's relation which may thus lead to the maximum percentage deviation from experimental values of the ultrasonic velocity.

An important reason for deviation is the molecular association effects that are not taken into account in these theories. This association is mainly due to hydrogen bond formation between like molecules. An associated molecular cluster in a liquid may be called as a quasi-molecule or a pseudo molecule. The present theories of liquids are inadequate to account comprehensively for the experimental manifestation of molecular interactions in various ultrasonic processes. It is obvious that the intermolecular interaction potential for a liquid will require for its full description; the knowledge of at least the dipole-dipole interactions, the collision factors, the hydrogen bond forces and the relative strengths of various interactions in like and unlike

molecules. Such a comprehensive expression for the intermolecular potential including all these factors has not yet been developed.

### CONCLUSION

It may be pointed out NR is best suited among the above theories for the prediction of ultrasonic velocity and hence molecular interaction in liquid mixtures. The chi-squared test values also support the NR theory.

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