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Theoretical evaluation of ultrasonic velocity and excess parameters in binary liquid mixture at 303k

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ABSTRACT

In earlier days it is possible for a scientist not only to master in his own field but also to have a working knowledge of all related fields. With the growth of scientific knowledge it became increasingly necessary to specialize in the theoretical and experimental investigation by putting much effort. Today very few are able to master even a single field like material science completely. This is because the physical behavior of a given material may be characterized by a set of macroscopic measurable quantities such as electrical conductivity, magnetic permeability, dielectric constant etc, and the chemical behavior like its reaction with different compounds. The material structures and contents may be achieved only if the scientist knows about theoretical background and technological aspects of the material to be studied. Hence the author tried to evaluate the theoretical parameters of the selected components when it is exposed to ultrasonic waves. In this study the chosen binary system is bromo benzene with O-xylene, M-xylene and P-xylene at different temperatures namely 293K, 303K, and 313K. The experimental values of ultrasonic velocity and density of binary mixtures of bromo benzene with O-xylene, M-xylene and P-xylene are taken from the work of P.S. Nigam et al and the sample selection is mainly due to the availability of the experimental data. Three methods namely Nomoto, Van deal and CFT are used for theoretical evaluation of ultrasonic parameters. The obtained results with different mole fraction are suitably interpreted using hydrogen bonding and dipole-dipole interaction. Also it reveals that Nomoto method is found to be suitable for theoretical evaluation of both binary mixtures.

Key words: Ternary mixture, Nomoto method, Van dael method,CFTmethod, Dipole-dipole interaction.

INTRODUCTION

With the growth of scientific knowledge, it became increasingly necessary to specialize in the theoretical and experimental investigation by putting much effort. The material structures and contents may be achieved only if the scientist knows about theoretical background and technological aspect of the materials to be studied. Hence it is decided to evaluate the theoretical parameters of the selected components when it is exposed to ultrasonic waves. The ultrasonic velocity measurements have been widely used to study the physical and chemical behavior of liquid mixtures. In recent years a good amount of work has been done to correlate the experimental ultrasonic velocities

with those computed theoretically using empirical and semi-empirical relations [1-5] Nomoto and bhimseenachel et al made successful attempts to evaluate the sound velocity on binary liquid mixtures. Van Deal ideal mixing relation has also been carried out successfully to investigate the acoustical behavior of binary liquid mixtures. The free length theory (FLT) of Jacobson and Schaff's pollution factor theory(CFT) have been used to predict the intermolecular interactions between unlike molecules of the mixtures by several workers[6-8]. They have found the FLT was better than CFT. For theoretical evaluation of sound velocity, other researcher [9] found that Van-Deal ideal mixing relation gives minimum deviation from the experimental values. In this context a comparative study of relative merits of the different methods becomes essential and the present work has been an attempt in this direction. The calculations were based on the experimental results taken from the work of P.S. Nikam et al[10]

THEORETICAL CONSIDERATIONS

Nomoto [11] suggested an empherical formula for sound velocity in binary liquid mixture as follows

$U_m = [(X1\ R1+X2\ R2)/(X1\ V1+X2\ V2)]^3$

Van Deal and Vangeal [12] suggested the following relation for sound velocity U_{im} as

$$\frac{1}{X_1M_1 + X_2M_2} \quad \frac{1}{U(im)^2} = \frac{X_1}{M_1U_1^2} + \frac{X_2}{M_2U_2^2}$$

Jacobson's relation [13] for sound velocity using the concept of intermolecular free length(L_f) is given by,

$U=K/ L_{f(mix)}(\rho mix)^{1/2}$

Schaff's [14] developed and expansion for sound velocity in Binary mixtures as

$$U_{mix} = \frac{U\infty\ (X_1S_1 + X_2S_2)\ (X_1B_1 + X_2B_2)}{Vm}$$

The symbol's used in all three relations have their usual meaning.

The values of excess thermodynamic parameters, G^E were evaluated from the relations

$G^E = G - G_{idl}$ here G_{idl} is the ideal value given by

$G_{idl} = X_1\ G_1 + X_2\ G_2$

The degree of intermolecular attraction (α) is given by $\alpha = (U_{xp}^2/\ U_{im}^2)-1$

The symbols used in all four relations have their usual meaning.

Excess parameters

Values [14] of the excess thermodynamic parameters G_E were evaluated from the relation.

$G_E = G - G_{idl}$

Here G_{idl} is the ideal value given by

$G_{idl} = \Sigma i\ X_i\ G_i$

The degree of intermolecular attraction is given by

$\alpha = (U^2_{exp} / U^2_{im}) – 1$

RESULTS AND DISCUSSION

The values of sound velocity have been evaluated theoretically using three different methods. The binary system chosen for the study is bromo benzene with O-xylene, M-xylene and P-xylene at temperatures 293 k, 303k and 313k. the experimental and theoretical values of ultrasonic velocity and the percentage deviation of theoretical velocity from the experimental values in the above mixtures for different mole fractions of bromo benzene at the temperature 303K were reported in tables (1 to 3) and the same trend is observed with other temperatures. The variation of velocity with concentration of bromo benzene is reported graphically in Fig. 1 to 3.
The values of sound velocity have been evaluated theoretically using three different methods namely Nomoto , Van-dael and CFT. The selected mixtures for analysis can be classified as

1. Polar in weakly polar mixtures.
2. Polar in non polar mixtures.

In all the three mixtures the increase of bromo benzene concentration in the solution decreases the ultrasonic velocity. It may be due to the fact that the denser molecules of bromo benzene affect the propagation of ultrasonic waves through the solution. Further it is also observed in the other selected temperature values.

1. Polar in weakly polar mixtures

Bromo benzene in O-xylene and M-xylene was the best example for this type of mixtures. Since they have got low dipole moment of 0.62 and 0.37 it can be considered as weakly polar compound. The results obtained from the table (1 to3) shows that there will be weak dipole – dipole interaction between bromo benzene with O-xylene and M-xylene. In all the three temperatures 293K, 303K and 313K, it shows positive deviations using different methods like Nomoto, Van-dael and CFT. While Nomoto and CFT method shows only small deviation, the Van-dael shows large deviation. The percentage in deviation increases first and then decreases with increase of mole fraction. Based on the above results it is worth wise to state that Nomato method yields the best results in all the cases. The CFT method also shows good results whereas the results obtained from Van dael method were not found to be satisfactory. The calculated value of U^2_{exp} / U^2_{idl} excess velocity, excess volume and excess impedance are given in the tables (4 to 6). From the table it is observed the values of alpha, excess velocity, excess volume and excess impedance are found to be mostly negative. The negative excess parameter indicates that there may be interstitial accommodation of bromo benzene molecules in aggregative of alkenes. The negative excess volume indicates the formation of molecular clusters and complexes. It may also indicate that they may involve in charge transfer complexes [15]. The negative excess sound velocity varies with mole fractions may be attributed to the breaking of both the hydrogen bonding and bipolar interaction on mixing

Table 1. Ultrasonic velocity and percentage deviation of binary mixture bromobenzene + o-xylene at 303k

Mole Fraction "X_1"	Density ρ_{mix} kgm^{-3}	Ultrasonic Velocity				Percentage Deviation		
		U expt ms^{-1}	Unomoto ms^{-1}	Uvan-deal ms^{-1}	Ucft ms^{-1}	(ΔU/U)% Nomoto	(ΔU/U)% Van-deal	(ΔU/U)% CFT
0.1135	939.34	1307.3	1305.4	1297.6	1304.3	0.14	0.74	0.23
0.2236	1006.69	1288.5	1286.1	1272.2	1283.8	0.19	1.26	0.36
0.3306	1072.14	1269.8	1266.0	1249.4	1263.8	0.29	1.60	0.47
0.4344	1135.64	1251.0	1247.8	1228.4	1244.3	0.25	1.81	0.54
0.5354	1197.42	1232.3	1229.0	1210.3	1225.4	0.27	1.78	0.56
0.6335	1257.51	1213.5	1210.4	1193.2	1207.2	0.26	1.67	0.52
0.7289	1315.87	1194.8	1191.9	1177.7	1189.3	0.24	1.42	0.45
0.8217	1372.63	1176.0	1173.7	1163.7	1171.9	0.20	1.05	0.35
0.9121	1428.83	1157.3	1155.6	1150.5	1155.0	0.15	0.58	0.20

2. Polar in Non polar mixtures

Bromo benzene in P-xylene belongs to this category, since P-xylene has zero dipole moment. It was observed that average percentage deviation of the computed ultrasonic velocity using various methods shows only positive values. While Nomoto and CFT method shows only a small deviation, the Van-dael method shows large deviation. The percentage deviation increases first and then decreases with increase in mole fraction for all the methods. The percentage deviation can be studied on the basis of interation between the components of mixtures. Normally in polar and non polar mixtures there is dipole induced – dipole interaction which is very weak. Bromo benzene is having associative nature through hydrogen bonding. The missing of bromo benzene With non polar P-xylene may

result in the breaking of hydrogen bond there by promoting dissociation. The positive deviation observed is due to the molecular association and complex formation of molecules. The magnitude of deviation also depends on concentration. The calculated values of alpha, excess velocity, excess volume and excess impedance are all found to be mostly negative.

Table 2. Ultrasonic velocity and percentage deviation of binary mixture bromobenzene + m-xylene at 303K

Mole Fraction "X_1"	Density ρ_{mix} kgm^{-3}	Ultrasonic Velocity				Percentage Deviation		
		U expt ms^{-1}	Unomoto ms^{-1}	Uvan-deal ms^{-1}	Ucft ms^{-1}	(ΔU/U)% Nomoto	(ΔU/U)% Van-deal	(ΔU/U)% CFT
0.1135	924.71	1285.7	1284.1	1276.1	1282.8	0.12	0.74	0.22
0.2236	995.13	1269.3	1267.2	1253.1	1264.8	0.16	1.28	0.35
0.3306	1063.22	1253.0	1250.5	1232.7	1247.4	0.19	1.62	0.44
0.4344	1128.73	1236.6	1234.0	1214.9	1229.9	0.21	1.76	0.54
0.5354	1192.42	1220.3	1217.6	1198.6	1213.6	0.22	1.78	0.54
0.6335	1253.85	1203.9	1201.3	1184.1	1197.4	0.22	1.64	0.54
0.7289	1316.04	1187.6	1185.2	1167.8	1181.9	0.20	1.66	0.47
0.8217	1371.23	1171.2	1169.2	1159.2	1166.9	0.17	1.03	0.37
0.9121	1427.36	1154.9	1153.3	1148.3	1152.6	0.14	0.57	0.19

Table 3. Ultrasonic velocity and percentage deviation of binary mixture bromobenzene + p-xylene at 303K

Mole Fraction "X_1"	Density ρ_{mix} kgm^{-3}	Ultrasonic Velocity				Percentage Deviation		
		U expt ms^{-1}	Unomoto ms^{-1}	Uvan-deal ms^{-1}	Ucft ms^{-1}	(ΔU/U)% Nomoto	(ΔU/U)% Van-deal	(ΔU/U)% CFT
0.1135	920.67	1275.8	1274.3	1266.3	1273.0	0.12	0.74	0.21
0.2236	991.82	1260.5	1258.6	1244.6	1255.9	0.15	1.26	0.36
0.3306	1060.49	1245.3	1243.0	1225.5	1239.4	0.18	1.59	0.47
0.4344	1126.97	1230.0	1227.6	1208.4	1223.7	0.20	1.76	0.51
0.5354	1191.07	1214.8	1212.3	1193.3	1208.3	0.20	1.76	0.53
0.6335	1253.02	1199.5	1197.1	1179.9	1193.5	0.20	1.63	0.50
0.7289	1312.85	1184.3	1182.1	1168.0	1178.8	0.18	1.37	0.46
0.8217	1370.92	1169.0	1167.1	1157.2	1164.9	0.16	1.01	0.36
0.9121	1427.24	1153.8	1152.4	1147.0	1151.6	0.12	0.58	0.19

X_1 refers the mole fraction of Bromo benzene

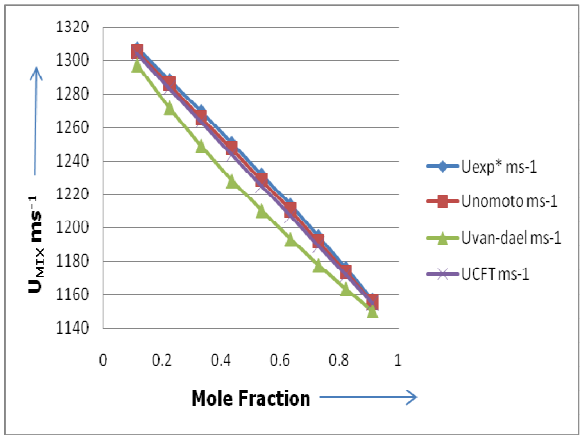

Fig. 1. Comparison of experimental value of U_{Mix} with theoretical value of bromo Benzene + O – Xylene – 303 K

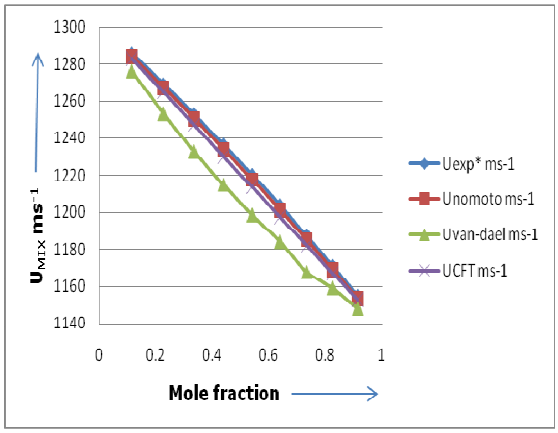

Fig.2. Comparison of experimental value of U_{mix} with theoretical value of bromo Benzene + M-Xylene – 303K

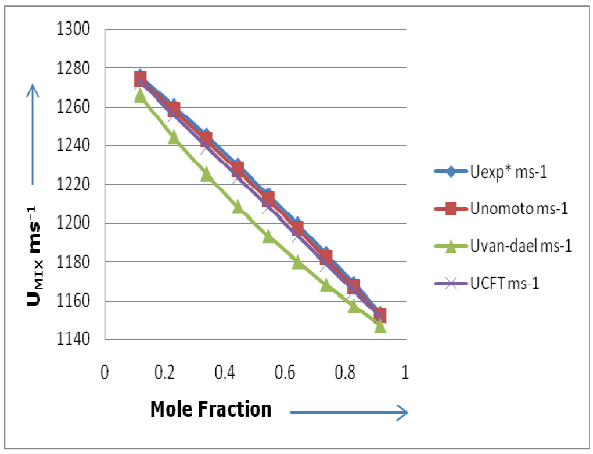

Fig 3. Comparison of experimental value of U_{mix} with theoretical value of bromo Benzene + P-Xylene – 303K

Table 4. Excess parameters in binary mixture bromobenzene +o-xylene at 303K

Mole Fraction "X_1"	Ultrasonic velocity U_{idl} ms^{-1}	U_{exp}^2/U_{idl}^2	Alpha	Excess Velocity(U^E) ms^{-1}	Excess Impedance (Z^E)10^3 Kg m^{-2}S^{-1}	Excess Volume (V^E) 10^{-3} m^3 mol^{-1}
0.1135	**1304.6**	**1.0041**	**0.0041**	**-72.34**	**-170.11**	**-0.31**
0.2236	**1283.9**	**0.0071**	**-0.9929**	**-51.69**	**-121.57**	**-0.17**
0.3306	**1263.9**	**0.0093**	**-0.9907**	**-31.63**	**-74.38**	**-0.07**
0.4344	**1244.4**	**0.0106**	**-0.9894**	**-12.17**	**-28.61**	**-0.01**
0.5354	**1225.5**	**0.0111**	**-0.9889**	**6.77**	**15.92**	**0.00**
0.6335	**1207.2**	**0.0104**	**-0.9896**	**25.03**	**58.87**	**-0.03**
0.7289	**1189.3**	**0.0091**	**-0.9909**	**42.92**	**100.93**	**-0.09**
0.8217	**1171.9**	**0.0070**	**-0.9930**	**60.32**	**141.85**	**-0.19**
0.9121	**1155.0**	**0.0039**	**-0.9961**	**77.27**	**182.50**	**-0.33**

The negative excess parameter indicated that there may be interstitial accommodation of bromo-benzene molecules in aggregate if alcohols. The negative excess volume indicates the formation of moleculer clusters & complexes and may involve in charge transfer complexes[16]. The negative excess sound velocity vary with mole fraction may be attribute to the breaking of both the hydrogen bond and bipolar interaction on mixing[17]. In general the obtained results indicate that there is some interaction between bromo-benzene and xylene. The interaction may be long range electrostatic attraction or weak hydrogen bonding. The interaction is weak because of steric hindrance, due to CH_3 group which is highly negative. In the presence of external field the interaction is found to be weak for all the individual rotation of molecules. The pair as such as not rotating as a singe unit. the molecular dipoles rotate in opposite directions due to which the values of velocity are continuously decreasing

Table 5. Excess parameters in binary mixture bromobenzene +m-xylene at 303K

Mole Fraction "X_1"	Ultrasonic velocity U_{idl} ms^{-1}	U_{exp}^2/U_{idl}^2	Alpha	Excess Velocity(U^E) ms^{-1}	Excess Impedance $(Z^E)10^3$ $Kg\ m^{-2}S^{-1}$	Excess Volume (V^E) $10^{-3}\ m^3\ mol^{-1}$
0.1156	1283.0	1.0042	0.0042	-62.72	-146.37	-0.31
0.2273	1264.8	0.0071	-0.9929	-44.59	-104.05	-0.16
0.3353	1247.3	0.0091	-0.9909	-27.06	-63.15	-0.07
0.4396	1230.0	0.0108	-0.9892	-9.75	-22.74	-0.01
0.5406	1213.6	0.0110	-0.9890	6.64	15.49	0.00
0.6383	1197.5	0.0107	-0.9893	22.74	53.07	0.03
0.7330	1185.9	0.0027	-0.9973	34.32	80.09	-0.09
0.8247	1167.0	0.0072	-0.9928	53.22	124.20	-0.19
0.9137	1152.6	0.0039	-0.9961	67.64	157.85	-0.33

Table 6. Excess parameters in binary mixture bromobenzene + p-xylene at 303K

Mole Fraction "X_1"	Ultrasonic velocity U_{idl} ms^{-1}	U_{exp}^2/U_{idl}^2	Alpha	Excess Velocity(U^E) ms^{-1}	Excess Impedance $(Z^E)10^3$ $Kg\ m^{-2}S^{-1}$	Excess Volume (V^E) $10^{-3}\ m^3\ mol^{-1}$
0.1162	1273.2	1.0041	0.0041	-58.40	-136.00	-0.31
0.2283	1256.1	0.0071	-0.9929	-41.31	- 96.19	-0.16
0.3365	1239.6	0.0092	-0.9908	-24.80	-57.76	-0.07
0.4411	1223.7	0.0103	-0.9897	-8.98	-20.92	-0.01
0.5421	1208.3	0.0107	-0.9893	6.42	14.95	0.00
0.6397	1193.4	0.0102	-0.9898	21.30	49.61	-0.03
0.7341	1178.9	0.0091	-0.9909	35.83	83.44	-0.09
0.8256	1165.0	0.0069	-0.9931	49.78	115.93	-0.20
0.9142	1151.6	0.0038	-0.9962	63.17	147.09	-0.33

CONCLUSION

In this paper the theoretical evaluation of ultrasonic velocity for binary mixture has been made. The work gives very interesting results and out of three different methods, the Nomoto method is found to be the best for both binary mixtures due to the closeness in values obtained with respect to the experiment.

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