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Research Article

THEORETICAL EVALUATION OF ULTRASONIC VELOCITY IN THE TERNARY LIQUID MIXTURES OF AMIDE + BENZENE + AMINES AT 303K

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ABSTRACT

The theoretical ultrasonic velocity in ternary mixtures of amide in benzene with amines at 303K have been evaluated by using theoretical models of liquid mixtures such as, Nomoto's relation, Free Length Theory, Ideal mixture relation, Junjie's method, Impedance dependence relation and Rao's relation. Ultrasonic velocity of these mixtures has been measured as a function of mole fraction and the experimental values are compared with theoretical values. The results are interpreted in terms of percentage deviation and intermolecular associations between the component molecules in the form of Hydrogen bonding.

Keywords: ternary liquid mixtures, multicomponent, theoretical models, molecular associations.

1. INTRODUCTION

Present investigation makes a comparative study of experimental ultrasonic velocity with six different theoretical models. Significant amount of work has been carried out[1-4]in investigating liquid state properties by ultrasonic velocity measurement which provides a very convenient and efficient pathway for determining several thermodynamical properties of liquid mixtures. Literature survey[5-7]reveals that previous workers have evaluated acoustical properties which are calculated from the measurement of velocity, density and viscosity. In the present study, Nomoto's relation[8], Free Length Theory[9], Ideal mixture relation[10], Junjie'srelation[11], Impedance dependence relation[12] and Rao's Relation[13] has been employed for the theoretical computation of ultrasonic velocity.

2. EXPERIMENTAL

For the present study chemicals (AR grade) were purchased from E-Merck with of minimum assay of 99.9%. Liquid mixtures of different composition were prepared in terms of mole fraction. Ultrasonic velocity of all the two ternary liquid mixtures has been measured using a single crystal ultrasonic interferometer with an operating frequency of 2-MHz supplied by M/s. Mittal Enterprises, New Delhi. Experimental temperature (303K) maintained using an electronically operated constant temperature water bath (Model B206, Sl.No: 003479, supplied by (Gemini Scientific Instruments, Chennai – 600 098, India) having accuracy ± 0.01°C, operating in the temperature range of 5°C to 120°C has been used to circulate water through the outer jacket of the double - walled measuring cell containing the experimental liquid. The density of all compounds was measured by a 10 ml specific gravity bottle calibrated with double distilled water and acetone. An Ostwald's viscometer with 10ml capacity was used for the viscosity measurements of all the compounds. The flow time of water and the flow time of solution were measured by a digital stop clock supplied by RACER with an accuracy of 0.01s.

3. THEORY

A number of mathematical equations have been proposed by many researchers for the computation of ultrasonic velocity for multi component systems. In the present paper the following equations are used, they are;

3.1 Nomoto'sRelation

Nomoto derived a relation[8] to evaluate ultrasonic velocity for a multicomponent liquid solutions and which can be expressed as,

$$U_{NR} = \left(\frac{\sum X_i R_i}{\sum X_i V_i}\right)^3$$

Where,X_i, R_i and V_i are the mole fraction, molar sound velocity and molar volume of the i^{th}component of the mixture.

3.2 Free Length Theory

Free length theory was established by Jacobson's[9] for ultrasonic velocity and which is calculated using the following formula as:

$$U_{FLT} = \left(\frac{K}{L_{f_{mix}} \rho_{mix}^{1/2}}\right)$$

Where K is Jacobson's constant and depends only on temperature $L_{f(mix)}$ and $\rho_{(mix)}$ are the intermolecular free length and density of the mixtures respectively.

3.3 Ideal Mixing Relation

The ideal mixing theory advanced by Van Dael and Vangeel[10] in the light of assumptions made by Blandermer and Waddington, yield the following relation for ultrasonic velocity in liquid mixtures as:

$$\left(\frac{1}{\Sigma X_i}\right)\left(\frac{1}{U_{IM}^2}\right) = \sum \frac{X_i}{M_i U_i^2}$$

Where,U_{IM} is the ideal mixing ultrasonic velocity in liquid mixture. $U_i$ultrasonic velocity in species. Another useful parameter, αdegree of molecular interaction parameter, which is a measure of the non ideality of the system, has been calculated using the relation.

3.4 Junjie's Relation

The Junjie's relation[11]for the determination of ultrasonic velocity for the multicomponent mixtures can be written as,

$$U_{JR} = \left(\sum_{i=1}^{n} x_i V_{mix}\right)\left(\sum_{i=1}^{n} x_i M_i\right)^{\frac{1}{2}}\left[\frac{(\sum_{i=1}^{n} x_i V_{mix})}{(\sum_{i=1}^{n} \rho_i U_i^2)}\right]^{\frac{1}{2}}$$

The symbols have their usual significances.

3.5 Impedance Dependence Relation

The sound speed in the mixture is given by Impedance dependence relation[12]as:

$$U_{IDR} = \left(\frac{\sum X_i Z_i}{\sum X_i \rho_i}\right)$$

Where,X_i, ρ_i and Z_i are the mole fraction, density and acoustic impedance of the i^{th} component of the mixture.

3.6 Rao's Relation

Rao's relation[13] is also called as specific sound velocity and can be expressed as

$$U_{RR} = (\Sigma X_i r_i \rho_i)^3$$

Where,$r_i$is the Rao's specific sound velocity of the i^{th}component of the mixture.

4. RESULT AND DISCUSSION

In the present study, two multicomponent (ternary) systems have been taken, and the liquids are mixed in the following manner,

System-I

N, N-DMF+Benzene+ Di-methylamine

System-II

N, N-DMF+ Benzene + Di-ethylamine

The experimentally determined and literature values of density (ρ) and ultrasonic velocity (U) at 303K of the pure components are listed in Table-1. And the thermodynamical and acoustical parameters required for this study has been taken from our previous work[14] and which has been displayed in Table-2.

The computed values of theoretical ultrasonic velocity of the various theories are shown in Table 3-4 and which shows deviations when it compared with the experimental data. From the Table-2 it is very clear that the density, viscosity, and velocity of the liquid mixtures are constantly increases with the addition of amines. This indicates that the presence of molecular interaction between the component molecules. (i.e., Amide and benzene) N, N - Dimethylformamide is the organic solvent widely used in binary and ternary liquid systems,

and it is a polar aprotic in nature[15]. When this is mixed with benzene, there is dipole-dipole interaction between N, N - Dimethylformamide and benzene[16].

From the first concentration onwards amines are introduced because it behaves as Lewis bases since they contain nitrogen as the basic center with lone pair of electrons. Aromatic amines also contain π electrons [17], but these electrons are used for resonance and it forms hydrogen bonding between amides.

Donor - Acceptor complexes expected between benzene and N,N-Dimethyl formamide that is possible because of π electron clouds in benzene can be donated to $C^{\delta+}$ of N, N - Dimethylformamide. In addition, when amines are introduced in between this, there is a possibility of intermolecular hydrogen bonding between carbonyl oxygen and Hydrogen in amine. Since such hydrogen is in between two highly electronegative elements. The C=O group is exhibiting negative inductive effect over the electron density of the hydrogen of amines. Therefore the possibility of forming intermolecular hydrogen bonding is greater. This holds good for the above two systems, because in Di-methyl and Di-ethyl amine nitrogen contains at least one hydrogen in its group.

Theoretical models are incorporated and responsible for molecules which are spherical in nature but it is not possible all time so it shows deviations. Nomoto's theory is based on additivity of molar sound velocity[18] and while mixing the liquids, the volume does not change but interaction is possible between the components of liquid mixtures like hydrogen bonding and dipole-dipole bonding[14]. Thus the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interaction is taking place between the component molecules in the liquid mixtures. Likewise ideal mixing relation is based on the assumption of the ratios of specific heats of ideal mixtures and the volumes are also equal[2]. The Values of experimental and theoretical values of ultrasonic velocity and percentage of deviation of the two ternary mixtures computed for six different models at 303K and which are displayed in Tables 3-6.

System-I FromTable-3 it is clear that theoretically evaluated velocity of the ternary liquid mixtures increases with decreasing mole fraction of Di-methyl amine. Calculated values of velocity show the same trend as observed experimentally. And from Table-5 it is evident that the ultrasonic velocities calculated by Nomoto's relation deviated from -2.3036 to 0.2399, Free length theory deviated from -1.3300 to -1.3321, Ideal mixing relation is deviated from -2.8321to 0.8260, Junjie's relation is deviated from 3.6170 to 10.9832, Impedance dependence relation shows deviation from -5.8200 to -0.4510 and Rao's relation is deviated from -6.9309 to 0.8258. The α values are found to be positive for first two concentration and which indicated that the strong interaction and rest of the values are in negative which indicates the that the weak interactions between the component molecules. The overall comparison of percentage deviation of this system shows the following trend:

$$U_{(JR)} > U_{(RR)} > U_{(IDR)} > U_{(IMR)} > U_{(NR)} > U_{(FLT)}$$

System-II FromTable-4 it is clear that theoretically evaluated velocity of the ternary liquid mixtures increases with decreasing mole fraction of Di-ethyl amine. Calculated values of velocity show the same trend as observed experimentally. And From Table-6 it is evident that the ultrasonic velocities calculated by Nomoto's relation deviated from -1.5533 to 6.7288, Free length theory deviated from -1.3301 to -1.3317, Ideal mixing relation is deviated from -0.8780 to 6.9595, Junjie's relation is deviated from -6.3214 to 6.7800, Impedance dependence relation shows deviation from -0.7914 to 6.8986 and Rao's relation is deviated from -1.5202 to 6.8431. The α value of the last concentration only negative and which shows weak interaction and the values from first concentration to seventh concentration shows positive, which indicated that the strong interaction between the component molecules. The overall comparison of percentage deviation of this system shows the following trend:

$$U_{(IMR)} > U_{(IDR)} > U_{(RR)} > U_{(JR)} > U_{(NR)} > U_{(FLT)}$$

5. CONCLUSION

Experimental data of ultrasonic velocity of the liquid mixtures of amide with amines in benzene have been compared with the above six theoretical models at 303K. And the comparisons are based on percentage of deviation. The deviation hold good for free length theory and Nomoto's Relation. The present study reveals that, out of six theories and relation, free length theory is best suited for the both multicomponent systems. From the values of degree of molecular interaction, it is concluded that there exists molecular interaction between component molecules and the interactions are maximum in

the second system when comparing with the first system.

Table 1: Values of density (ρ) and ultrasonic velocity (U) of pure liquids at 303K

Liquids	Density		Velocity	
	Exp.	Lit.	Exp.	Lit.
N,N-Dimethylformamide	948.0	947.6[19]	1246.0	1459.6[19]
Benzene	863.8	862.9[20]	1291.0	1285.0[20]
Di-methylamine	887.0	-	1674.0	-
Di-Ethylamine	705.0	-	1455.3	-

Table 2:Values of density (ρ), Viscosity (η) and ultrasonic velocity (U) of pure liquids at 303K

Mole fraction		Density	Viscosity	Velocity	Density	Viscosity	Velocity
x_1	x_3	Kgm^{-3}	$10^{-3}Nsm^{-2}$	ms^{-1}	Kgm^{-3}	$10^{-3}Nsm^{-2}$	ms^{-1}
		N,N-DMF + Benzene + Di-methylamine			N,N-DMF + Benzene + Di-Ethylamine		
0.000	0.700	816.80	0.7001	1354.70	810.90	0.6892	1351.90
0.100	0.600	826.80	0.7495	1358.40	813.80	0.7281	1354.70
0.200	0.500	831.40	0.8612	1364.70	822.60	0.7992	1360.40
0.300	0.400	834.70	0.9465	1369.30	829.60	0.8678	1367.80
0.400	0.300	839.70	1.1092	1372.70	836.80	1.0457	1371.40
0.500	0.200	844.30	1.3327	1377.50	846.80	1.3047	1375.20
0.600	0.100	848.40	1.4251	1386.40	856.20	1.4057	1382.60
0.700	0.000	857.40	1.5684	1392.60	868.10	1.5238	1387.80

Table 3:Values of Experimental and theoretical values of ultrasonic velocity (U) of N,N-Dimethylformamide + Benzene + Di - methylamine at 303K

Mole fraction	$U_{(EXP)}$	$U_{(NR)}$	$U_{(FLT)}$	$U_{(IMR)}$	$U_{(JR)}$	$U_{(IDR)}$	$U_{(RR)}$
X	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}
0.000	1354.70	1351.45	1372.72	1346.35	1205.91	1360.81	1377.18
0.100	1358.40	1360.20	1376.49	1347.18	1225.86	1376.95	1418.61
0.200	1364.70	1367.46	1382.85	1379.13	1245.67	1390.80	1353.43
0.300	1369.30	1377.27	1387.53	1384.00	1265.49	1407.08	1385.72
0.400	1372.70	1388.29	1390.98	1385.55	1285.17	1424.02	1436.17
0.500	1377.50	1398.72	1395.85	1411.42	1304.48	1439.78	1412.94
0.600	1386.40	1411.70	1404.86	1412.67	1323.19	1457.09	1477.40
0.700	1392.60	1424.68	1411.13	1432.04	1342.23	1473.65	1489.12

Table 4:Values of Experimental and theoretical values of ultrasonic velocity (U) N, N-Dimethylformamide + Benzene + Di-ethylamine at 303K

Mole fraction	$U_{(EXP)}$	$U_{(NR)}$	$U_{(FLT)}$	$U_{(IMR)}$	$U_{(JR)}$	$U_{(IDR)}$	$U_{(RR)}$
X	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}
0.000	1351.9	1260.93	1369.88	1257.82	1260.24	1258.64	1259.39
0.100	1354.7	1284.96	1372.74	1276.59	1291.52	1275.09	1275.29
0.200	1360.4	1308.42	1378.50	1288.89	1323.29	1292.90	1315.25
0.300	1367.8	1331.05	1386.01	1315.29	1355.09	1312.08	1316.67
0.400	1371.4	1351.12	1389.66	1329.36	1384.40	1330.92	1352.48
0.500	1375.2	1372.07	1393.50	1355.61	1416.06	1352.85	1362.26
0.600	1382.6	1391.05	1401.00	1369.55	1445.85	1374.94	1408.28
0.700	1387.8	1409.36	1406.27	1399.99	1475.53	1398.78	1408.90

Table 5:Values of Percentage deviation between experimental and theoretical values of ultrasonic velocity (U) and Degree of molecular interaction (α) of N, N-Dimethylformamide + Benzene + Di - methylamine at 303K

Mole fraction	$\%U_{(NR)}$	$\%U_{(FLT)}$	$\%U_{(IMR)}$	$\%U_{(JR)}$	$\%U_{(IDR)}$	$\%U_{(RR)}$	α
X	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	
0.000	0.2399	-1.3302	0.6164	10.9832	-0.4510	-1.6594	0.0124
0.100	-0.1325	-1.3317	0.8260	9.7571	-1.3656	-4.4324	0.0167
0.200	-0.2022	-1.3300	-1.0574	8.7221	-1.9125	0.8258	-0.0208
0.300	-0.5820	-1.3313	-1.0735	7.5812	-2.7591	-1.1992	-0.0211
0.400	-1.1357	-1.3317	-0.9361	6.3765	-3.7386	-4.6237	-0.0185
0.500	-1.5405	-1.3321	-2.4624	5.3009	-4.5212	-2.5728	-0.0475
0.600	-1.8249	-1.3315	-1.8948	4.5593	-5.0988	-6.5638	-0.0368
0.700	-2.3036	-1.3306	-2.8321	3.6170	-5.8200	-6.9309	-0.0543

Table 6:Values of Percentage deviation between experimental and theoretical values of ultrasonic velocity (U) and Degree of molecular interaction (α) of N, N-Dimethylformamide + Benzene + Di - ethylamine at 303K

Mole fraction	$\%U_{(NR)}$	$\%U_{(FLT)}$	$\%U_{(IMR)}$	$\%U_{(JR)}$	$\%U_{(IDR)}$	$\%U_{(RR)}$	α
X	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	
0.000	6.7288	-1.3301	6.9595	6.7800	6.8986	6.8431	0.1552
0.100	5.1480	-1.3317	5.7661	4.6638	5.8766	5.8619	0.1261
0.200	3.8209	-1.3301	5.2568	2.7279	4.9620	3.3189	0.1140
0.300	2.6871	-1.3314	3.8390	0.9292	4.0739	3.7384	0.0814
0.400	1.4785	-1.3315	3.0658	-0.9476	2.9517	1.3795	0.0643
0.500	0.2276	-1.3309	1.4244	-2.9714	1.6251	0.9409	0.0291
0.600	-0.6114	-1.3308	0.9441	-4.5746	0.5542	-1.8572	0.0192
0.700	-1.5533	-1.3307	-0.8780	-6.3214	-0.7914	-1.5202	-0.0173

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