

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.

IndexTerms - ternary liquid mixtures, multicomponent, theoretical models, molecular associations, percentage deviation

1. Introduction:

Present investigation makes a comparative study of experimental ultrasonic velocity with six different theoretical models. Significant amount of work has been carried out¹⁻⁴ in investigating liquid state properties by ultrasonic velocity measurement which provides a very convenient and efficient pathway for determining several thermo dynamical properties of liquid mixtures. Literature survey⁵⁻⁷ 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 relation⁸, Free Length Theory⁹, Ideal mixture relation¹⁰, Junjie's relation¹¹, Impedance dependence relation¹² and Rao's Relation¹³ 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 a 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 2MHz supplied by M/s. Mittal Enterprises, New Delhi. 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 used are

3.1 Nomoto's Relation:

Nomoto derived a relation⁸ 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's⁹ for ultrasonic velocity 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 it 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 Vangeel¹⁰ in the light of assumptions made by Blandermer and Waddington, yield the following relation for ultrasonic velocity in liquid mixtures as

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

Where, U_{IM} is the ideal mixing ultrasonic velocity in liquid mixture. U_i ultrasonic velocity in species. Another useful parameter, α degree 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 relation¹¹ for the determination of ultrasonic velocity for the multi component mixtures can be written as

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

The symbols have their usual significances.

3.5 Impedance dependence relation:

The sound speed in the mixture is given by Impedance dependence relation¹² 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 relation¹³ is also called as specific sound velocity and can be expressed as

$$U_{RR} = (\sum X_i r_i \rho_i)^{\frac{1}{3}}$$

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. The thermodynamical and acoustical parameters required for this study has been taken from our previous work¹⁴ and which has been displayed in Table-2

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	
							Kgm^{-3}
x_1	x_3	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

The computed values of theoretical ultrasonic velocity from the various theories are shown in Table 3-4 which shows deviations when compared with the experimental data. From Table-2 it is very clear that the density, viscosity, and velocity of the liquid mixtures are constantly increasing with the addition of amines. This indicates the presence of molecular interaction between the component molecules (i.e., Amide and benzene). N, N - Dimethylformamide is an organic solvent widely used in binary and ternary liquid systems, and it is a polar aprotic in nature¹⁵. When this is mixed with benzene, there is dipole-dipole interaction between N, N - Dimethylformamide and benzene¹⁶.

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 electrons¹⁷, 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 is possible because of π electron clouds in benzene and 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 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 atleast one hydrogen in its group.

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

Mole fraction X	$U_{(EXP)}$ ms ⁻¹	$U_{(NR)}$ ms ⁻¹	$U_{(FLT)}$ ms ⁻¹	$U_{(IMR)}$ ms ⁻¹	$U_{(JR)}$ ms ⁻¹	$U_{(IDR)}$ ms ⁻¹	$U_{(RR)}$ 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 Experimental and theoretical values of ultrasonic velocity (U) N, N-Dimethylformamide + Benzene + Di-ethylamine at 303K

Mole fraction X	$U_{(EXP)}$ ms ⁻¹	$U_{(NR)}$ ms ⁻¹	$U_{(FLT)}$ ms ⁻¹	$U_{(IMR)}$ ms ⁻¹	$U_{(JR)}$ ms ⁻¹	$U_{(IDR)}$ ms ⁻¹	$U_{(RR)}$ 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 X	%U _(NR) ms ⁻¹	%U _(FLT) ms ⁻¹	%U _(IMR) ms ⁻¹	%U _(JR) ms ⁻¹	%U _(IDR) ms ⁻¹	%U _(RR) ms ⁻¹	α
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 X	%U _(NR) ms ⁻¹	%U _(FLT) ms ⁻¹	%U _(IMR) ms ⁻¹	%U _(JR) ms ⁻¹	%U _(IDR) ms ⁻¹	%U _(RR) ms ⁻¹	α
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

Theoretical models are incorporated and responsible for molecules which are spherical in nature but it is not possible all the time, so it shows deviations. Nomoto's theory is based on additivity of molar sound velocity¹⁸ 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 bonding¹⁴. 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 equal². 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 are displayed in Tables 3-6.

System-I From Table-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. 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 deviated from -2.8321 to 0.8260, Junjie's relation deviated from 3.6170 to 10.9832, Impedance dependence relation shows deviation from -5.8200 to -0.4510 and Rao's relation deviated from -6.9309 to 0.8258. The α values are found to be positive for first two concentration which indicate the strong interaction and rest of the values are negative which indicates that there is a weak interaction between the component molecules. The overall comparison of percentage deviation of this system is in the following trend

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

System-II From Table-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 deviated from -0.8780 to 6.9595, Junjie's relation deviated from -6.3214 to 6.7800, Impedance dependence relation shows deviation from -0.7914 to 6.8986 and Rao's relation deviated from -1.5202 to 6.8431. The α value of the last concentration is only negative which shows weak interaction and the values from first concentration to seventh concentration show positive value, which indicates the presence of strong interaction between the component molecules. The overall comparison of percentage deviation of this system is in 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 holds 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 both the multicomponent systems. From the values of degree of molecular interaction, it may be concluded that there exists molecular interaction between component molecules and the interactions are maximum in the second system when compared with the first system.

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