Theoretical evaluation of acoustical velocity in binary liquid mixtures of sulphate solutions

K.Rathina[a],C.Senthamilselvi[b],S.Umadevi[c] H.B.Ramalingam[d]

Abstract— The ultrasonic velocity, density and viscosity have been measured for the binary liquid mixtures of ammonium persulphate as common component with coppersulphate, ferrous ammonium sulphate, zinc sulphate, magnesisum sulphate at various concentrations at 303K.From the acoustical parameters like adiabatic compressibility,impedance which are calculated from ultrasonic velocity and other measured values. the theoretical values of ultrasonic velocity were evaluated using Nomoto's relation (U_{NOM}), ideal mixing relation (U_{IMR}), impedance relation (U_{IDR}), Jungie's relation (U_{JR}),. The theoretical and experimental ultrasonic velocities are compared. The validity of the theories is checked on the application of the chi-square test(x^2) for goodness of fit and by calculating the average percentage error (APE).An apperecible agreement has been found between experimental and theoretical ultrasonic velocities.

. **Index Terms —** Ammonium persulphate, copper sulphate, Nomotos relation, ultrasonic velocity, Junjie's relation

1 INTRODUCTION

Acoustical parameters of liquid mixtures and the non linearity in the physical properties are used to study molecular interactions and physico- chemical behaviour of liquid mixtures at various concentrations [1],[2],[3],[4],[5]. Theoretical evaluation of sound velocity in liquid mixtures are done by several relations and semi empirical formulas the comparision of theoretical velocities with experimental values is of very much important to study about the molecular interaction of liquid mixtures consisting of polar and non-polar components and also provides better understanding about the ultrasonic velocity [6],[7],[8],[9].

In our present study ammonium persulphate is chosen because of its industrial importance.It is a strong oxidizing agent and radical initiator. It is used to etch copper on printed circuit boards as an alternative to ferric chloride solution.It is also used along with tetra methyl ethylenediamine to catalyze the polymerization of acrylamide in making a polyacrylamide gel. It has also been utilized to study protein - protein interactions via photoinitiated crosslinking chemistry [10].

2 EXPERIMENTAL

The sulphates used are AR grade were obtained from Merk. The aqueous solutions of the salts were made by dissolving them in distilled water. Standard procedure was followed for measuring density by using specific gravity bottle of 10ml. Ostwalts viscometer is used for the viscosity of theosity measurements of liquid mixtures. Liquid mixtures at various concentrations are prepared.

Ultrasonic velocities in the two binary liquid mixtures have been measured using the ultrasonic liquid interferometer of frequency 2 MHz manufactured from Mittal enterprises at room temperature 303K with accuracy of ±.02%.

3 THEORETICAL

Experimental ultrasonic velocities are compared with the theoretically evaluated ultrasonic velocities which are obtained from the following relations

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

$$U_{NOM} = \left[\frac{(x_1R_1 + x_2R_2)}{(x_1V_1 +)x_2V_2)}\right]^3 \quad (1)$$

Where R_1, R2 are molar sound velocities, x_1 and x_2 are the mole fractions of 1st and 2nd components of the liquid mixtureand V_1, V_2 are molar volumes.

Van Deal and Vangeal [12] suggested an ideal mixing relation for ultrasonic velocityUIMR as

$$U_{IMR} = \left[\frac{1}{X_1M_1 + X_2M_2}\right]^{\frac{1}{2}}\left[\frac{X_1}{M_1U_1^2} + \frac{X_2}{M_2U_2^2}\right] \quad (2)$$

Where M_1, M_2 are molecular weights and U_1, U_2 are ultrasonic velocities of individualcomponents

The impedance relation[13]is

[a]DepartmenofPhysics,KumaraguruCollege of Technology,Coimbatore,India.
[b]. Department of Physics,Sathyabama University,Chennai,,India
[c]. Department of Physics,S.V.S. College of Technology, Coimbatore,India.
[d]Department of Physics,Government Arts college Udumalpet,India

$$U_{IDR} = \frac{X_1 Z_1 + X_2 Z_2}{X_1 \rho_1 + X_2 \rho_2} \quad (3)$$

3

ρ_1, ρ_2 are the densities and Z_1, Z_2 are the acoustic impedances

The Junjie equation[14] is given as

$$U_{JR} = \left(\frac{x_1 V_1 + x_2 V_2}{(x_1 M_1 + x_1 M_1)^{\frac{1}{2}}} \right) \left(\frac{x_1 M_1}{\rho_1 U_1^{\,2}} + \frac{x_2 M_2}{\rho_2 U_2^{\,2}} \right)^{\frac{-1}{2}} \quad (4)$$

Where 1& 2 represents the first and second component of the liquid mixture and the symbols used in the formulas have their usual meanings.

3 RESULTS AND DISCUSSION

From the experimental ultrasonic velocity and acoustical parameters theoretical ultrasonic velocities are computed using Nomoto'srelation [NOM], Ideal mixing relation [IMR], Impedance theory[IDR] and Junjie's relation [JR] for for the following the binary liquid mixtures at various concentrations and given inTable 1 :

1 ammonium per sulphate + copper sulphate
2 ammonium persulphate +ferrous ammonium sulphate
3 ammoniumpersulphate + Zinc sulphate
4 ammoniumpersulphate +ammoniumsulphate
5 ammoniumpersulphate + magnesium sulphate

Chi-Square test and Average Percentage Deviation(APE) are applied to test the validity of the theories.

Chi-Square test for goodness of fit

Chi- Square value is calculated from the formula [15]

$$x^2 = \sum_{i=1}^{n} \frac{\left(U_{\exp} - U_{theo}\right)^2}{U_{theo}} \quad (5)$$

Average Percentage Error (APE)

The average percentage Error [16] is calculated using the formula

$$APE = \frac{1}{n} \sum_{i=1}^{n} \frac{U_{\exp} - U_{theo}}{U_{\exp}} \times 100 \quad (6)$$

Where, n- number of data used.

$U_{\exp}$ = experimental values of ultrasonic velocities of mixtures.

U_{theo} = theoretically computed values of ultrasonic velocities of mixtures.

While mixing two liquids, the molecular interact ion between the liquids is due to the presence of dispersive force, charge transfer, hydrogen bonding and dipole induced dipole interactions.The deviation in the experimental and theoretical ultrasonic velocity shows the that molecular interactions takes place between unlike molecules.The deviation of experimental
values from values calculated using. Ideal mixing relation, may be because of compressibility of component liquids is present in the mixtures. The deviation of experimental values from values calculated using impedance relation, shows non additivity of acoustic impedance.The deviation in Junjie's relation is due to the molecular interaction takes place between unlike molecules in the liquid mixtures [17],[18]because of compressibility of component.percentage deviation is used to measure the non ideality in liquid mixtures. The percentage deviation and Average percentage error (APE) for theoretical ultrasonic velocities are shown in Table 2.

Average percentage error is minimum for Nomoto and Junjies relation than those obtained by other theories.Higher deviations shows the existence of strong tendancy for the association between component molecules as a result of hydrogen bonding[19].

The minimum deviation in the velocities obtained by Nomoto and Junjie's theory shows that theory holds good for self associated polar liquids [20] The results obtained for binary system shows that the CFT method is found to be best suitable for binary mixture due to closeness of the values observed with respect to the experiment.Suitable interpretations based on the molecular interaction, dipole-dipole interaction and H-bonding were given for the system.

3 CONCLUSION

Experimental and theoretical ultrasonic velocities are measured for five different liquid mixture systems at various concentrations at303K.After comparision of experimental values and theoretical values of ultrasound velocities it is clear that out of all the theories Nomoto theory provide good result.The deviation observed between experimental and theoretical exhibit the presence of intermolecular interactions in the above binary liquid mixture systems.

[a]DepartmenofPhysics,KumaraguruCollege of Technology,Coimbatore,India.
[b]. Department of Physics,Sathyabama University,Chennai,,India
[c]. Department of Physics,S.V.S. College of Technology, Coimbatore,India.
[d]Department of Physics,Government Arts college Udumalpet,India

TABLE 1

EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES FOR DIFFERENT SYSTEMS AT 303K.

Mole Fraction	Ultrasonic Velocity (U) ms^{-1}				
	Expt	NOM	IMR	IDR	JR
Ammoniumpersulphate+ coppersulphate					
0.1084	1574.4	1624.6	1578.1	1578.4	1578.0
0.2148	1578.4	1625.5	1583.8	1584.3	1583.5
0.3192	1579.2	1626.4	1589.4	1590.1	1589.1
0.4218	1583.4	1627.4	1595.0	1595.8	1594.7
0.5225	1592.6	1628.4	1600.7	1601.4	1600.3
0.6214	1603.3	1629.3	1606.3	1607.0	1605.9
0.7185	1605.9	1630.3	1611.9	1612.5	1611.5
0.8140	1611.0	1631.3	1617.5	1617.9	1617.2
0.9078	1615.8	1632.3	1623.0	1623.3	1622.9
Ammoniumpersulphate+ferrousammoniumsulphate					
0.1603	1681.0	1689.7	1649.1	1687.5	1688.8
0.3005	1677.3	1684.3	1622.4	1680.5	1682.6
0.4241	1666.3	1678.9	1608.0	1674.3	1676.8
0.5339	1651.3	1673.6	1601.8	1668.6	1671.3
0.6321	1652.7	1668.4	1601.4	1663.5	1666.0
0.7205	1638.5	1663.3	1605.1	1658.8	1661.1
0.8132	1641.0	1657.5	1613.2	1653.9	1655.6
0.8730	1639.7	1653.4	1620.8	1650.6	1651.9
0.9393	1628.3	1648.5	1631.6	1647.0	1647.7
Ammoniumpersulphate+ zinc sulphate					
0.1228	1617.2	1612.8	1609.1	1613.1	1612.7
0.2395	1631.6	1615.1	1608.9	1615.7	1614.9
0.3507	1634.0	1617.4	1609.7	1618.1	1617.2
0.4565	1634.0	1619.7	1611.3	1620.5	1619.5
0.5575	1631.2	1622.0	1613.6	1622.8	1621.7
0.6540	1649.6	1624.3	1616.6	1625.1	1624.0
0.7462	1642.8	1626.5	1620.1	1627.2	1626.3
0.8344	1662.0	1628.7	1624.0	1629.3	1628.6
0.9190	1663.2	1630.9	1628.4	1631.3	1630.9
Ammoniumpersulphate+ ammonium sulphate					
0.0604	1618.0	1624.6	1610.0	1624.2	1623.6
0.1265	1626.0	1625.5	1597.6	1624.8	1624.5
0.1988	1639.6	1626.4	1586.6	1625.5	1625.4
0.2785	1648.0	1627.4	1577.6	1626.3	1626.3
0.3677	1664.0	1628.4	1569.5	1627.2	1627.4
0.4648	1643.2	1629.3	1568.2	1628.2	1628.4
0.5747	1652.4	1630.3	1570.1	1629.2	1629.5
0.6985	1637.2	1631.3	1579.0	1630.4	1630.7
0.8390	1657.6	1632.3	1598.1	1631.7	1631.9
Ammoniumpersulphate+magnesium sulphate					
0.1071	1631.2	1638.5	1638.5	1638.8	1638.6
0.2126	1617.9	1641.1	1640.9	1641.4	1641.1
0.3164	1616.2	1643.6	1643.3	1644.0	1643.6
0.4186	1622.0	1646.1	1645.8	1646.6	1646.1
0.5192	1637.0	1648.6	1648.3	1649.1	1648.6
0.6183	1656.5	1651.2	1650.8	1651.6	1651.1
0.7159	1662.6	1653.7	1653.4	1654.1	1653.6
0.8120	1630.0	1656.2	1656.0	1656.5	1656.2
0.9067	1648.0	1658.8	1658.6	1658.9	1658.7

TABLE 2

% DEVIATION FOR THEORETICAL VELOCITIES FOR DIFFERENT SYSTEMS AT 303K.

ISSN 2229-5518

Molefraction	% deviation(ΔU/U %)			
	NOM	IMR	IDR	JR
Ammoniumpersulphate+ coppersulphate				
0.1084	-0.2300	-0.2339	-0.2519	-0.2255
0.2148	-0.3346	-0.3396	-0.3710	-0.3241
0.3192	-0.6387	-0.6434	-0.6853	-0.6227
0.4218	-0.7279	-0.7318	-0.7801	-0.7080
0.5225	-0.5018	-0.5070	-0.5551	-0.4822
0.6214	-0.1832	-0.1864	-0.2335	-0.1632
0.7185	-0.3691	-0.3734	-0.4126	-0.3525
0.8140	-0.3963	-0.3996	-0.4289	-0.3836
0.9078	-0.4448	-0.4484	-0.4629	-0.4393
x^2	0.2973	0.2375	0.3496	0.2798
APE	-0.4252	-0.4293	-0.4646	0.4112
Ammoniumpersulphate+ ferrousammonium sulphate				
0.1603	-0.5192	1.8956	-0.3855	-0.4645
0.3005	-0.4179	3.2713	-0.1946	-0.3198
0.4241	-0.7564	3.4992	-0.4786	-0.6301
0.5339	-1.3496	2.9996	-1.0471	-1.2068
0.6321	-0.9545	3.1038	-0.6563	-0.8093
0.7205	-1.5151	2.0414	-1.2409	-1.3773
0.8132	-1.0028	1.6949	-0.7839	-0.8903
0.8730	-0.8353	1.1492	-0.6687	-0.7480
0.9393	-1.2386	-0.2016	-1.1471	-1.1913
x^2	1.5089	9.1628	0.9530	1.2189
APE	-0.9544	2.1615	-0.73364	-0.8486
Ammoniumpersulphate+ zinc sulphate				
0.1228	0.2749	0.4994	0.2548	0.2807
0.2395	1.0114	1.3894	0.9771	1.0229
0.3507	1.0145	1.4865	0.9706	1.0288
0.4565	0.8737	1.3882	0.8245	0.8893
0.5575	0.5636	1.0776	0.5131	0.5801
0.6540	1.5356	2.0019	1.4881	1.5498
0.7462	0.9916	1.3840	0.9499	1.0032
0.8344	2.0017	2.2853	1.9697	2.0098
0.9190	1.9399	2.0913	1.9202	1.9425
x^2	2.4047	3.8622	2.2819	2.4401
APE	1.1341	1.5115	1.0964	1.1452
Ammoniumpersulphate+ ammonium sulphate				
0.0604	-0.4060	0.4924	-0.3809	-0.3457
0.1265	0.0305	1.7490	0.0723	0.0946
0.1988	0.8023	3.2341	0.8572	0.8691
0.2785	1.2503	4.2732	1.3147	1.3139
0.3677	2.1418	5.6767	2.2111	2.2013
0.4648	0.8446	4.5646	0.9155	0.9005
0.5747	1.3375	4.9797	1.4030	1.3855
0.6985	0.3613	3.5557	0.4154	0.3980
0.8390	1.5276	3.5886	1.5609	1.5485
x^2	2.0061	23.4066	2.1738	2.1443
APE	0.8766	3.5682	0.9299	0.9295
Ammoniumpersulphate+magnesium sulphate				
0.1071	-0.4497	-0.4481	-0.4660	-0.4554
0.2126	-1.4297	-1.4187	-1.4538	-1.4309
0.3164	-1.6946	-1.6786	-1.7237	-1.6941
0.4186	-1.4862	-1.4671	-1.5177	-1.4843
0.5192	-0.7108	-0.6907	-0.7420	-0.7078
0.6183	0.3208	0.3406	0.2922	0.3248
0.7159	0.5323	0.5509	0.5084	0.5375
0.8120	-1.6094	-1.5950	-1.6267	-1.6050
0.9067	-0.6535	-0.6444	-0.6615	-0.6496
x^2	1.8003	1.7694	1.8553	1.7981
APE	-0.7979	-0.7835	-08212	-0.7961

REFERENCES

[1] Dunlop R.D and Scott.R.L 1962 J.Phys.Chem 66 631
[2] Manoharamoorthy N and Subramaniyam S.V 1972 IndianJ.Pure appl.Phys.15 48
[3] G. K. Johari and R.C. Misra, Ind J pure and appl Phys, 29 (1991) 155-158
[4] Ali, A, Hyder, S and Nain A.K, J. Mol. Liquids, 1999, 79, 89
[5] Douheret G, Daris M.I, Fjellanger I.J and Hoiland H, J. Chem. Soc. Fraday Trans, 1997, 93,1943.
[6] Pandey J.D., Rajan Dey and Divited, D.K. Pramana, J.Phy, 52(1999)87.
[7] Jacobson B, Acta Chem., Phys., 19(1950) 927.
[8] N. Manohar Murthy et al, Acoustica, 48 (1981) 341.
[9] R. T. Longman and W.S. Dunbar, J Phys chem. 49 (1945) 428. Kalidoss S and Saivasamoorthy T, J. Pure Appl .Ultrason., 1997, 19, 9.
[10] David A Fancy Carilee Denison Kyonghee Kim Yueqing Xie, Terra Holdeman, Frank Amini, Thomas Kodadek, Chem. Biol., 7(9)697 708 (2000)
[11] Nomoto J.Phys..Soc, 13, (1958) 1528
[12] Van-Deal W (1978) Thermodynamics Properties and velocity of sound (London:Better Worth) Ch.5
[13] W. Schaaffs Z. phys 114 (1939) 110)
[14] Junjie Z., J china univ sci Tech 14 (1984) 298-300.
[15] Pearson K, Fundamentals of Mathematical Statistics, Eds. Gupta S G, Kapoor V K, S.Chand and Company, New Delhi, India, 1973, 903.
[16] (Jyh-Shing and Roger Jang, IEEE Trans Syst Man Cybern., 1993, 23(4), 665
[17] A Ali; AYasmin; A K Nain. Indian J Pure & Appl. Phys., 2002, 40, 315.
[18] Uvarani R and Punitha S, E-J. Chem., 2009, 6(S1), S235,
[19] Schaffs W, Z Phy, 1939, 114, 110, ibid, 1940, 115, 69.
[20] Anihotri P k and Adgaonkar CS, ultrasonics, 1989, 27,248.