Thermodynamic Behaviour of Ternary Mixtures of Acrylonitrile in Benzene with N-N-di methyl aniline at 303K, 308K and 313K

R. Chithra Devi [#1], R.Mathammal[2]

[#]*Department of Physics, N.K.R. Government Arts College for Women, Namakkal, Tamil Nadu*

[1]rajchithradevi@gmail.com

[2]mathammals_shanmugam@yahoo.com

***Abstract*— The density (ρ), viscosity and ultrasonic velocity (u) in ternary liquid mixture of acrylonitrile (AN) with benzene in N-N-di methyl aniline have been measured at (303,308 and 313)K respectively, over the entire composition range by using an ultrasonic interferometer for measuring velocity at 2MHz frequency. From the experimental data various acoustical and thermodynamical parameters such as; adiabatic compressibility(β), Intermolecular free length (L_f), Specific acoustic Impedance (Z), relative association(RA) and molar sound velocity have been computed using the standard relations. The results have been analysed on the basis of variation in thermodynamic parameters. These parameters are found to be very sensitive in exploring the interaction between the component molecules, which enable to have better understanding of the liquid mixtures.**

Since the system show similar trends for evaluated parameter so the constituent ternary mixture at different temperatures. The results have been interpreted in terms of dipole induced dipole interaction.

***Keywords* —** Ultrasonic **Velocity, Adiabatic compressibility, free length, free volume. Relaxation time**

I. INTRODUCTION

In recent years, the measurement of ultrasonic velocity has been successfully employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. Ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in liquid mixtures [1–3]. The significance of acoustic, volumetric and thermodynamic studies in mixtures have been used for understanding the intermolecular interaction by many researchers for interpreting different type of interactions viz dipole-dipole [4-6] and dipole induced dipole [7-10]; polar-polar [11,12] and polar-non polar[13,14] systems. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids and liquid mixtures. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components [15,16] .

Acrylonitrile is a versatile liquid, use in the polymer industry to produce acrylic fiber, acrylonitrile–butadiene–styrene resins, adiponitrile, nitrile rubbers, elastomers, styrene–acrylonitrile resins, etc., which have a variety of uses in the modern world. Thus, studies of the physicochemical properties of binary mixtures containing acrylonitrile have attracted considerable interest [17–19]. Aniline molecule is highly polar and self associated through hydrogen bonding of their amine group. Being aromatic, aniline with amino group is comparatively a strong electron donor. The H atoms in the NH_2 group can also play the role of electron-acceptors centres [20]. It is used in manufacturing of synthetic dyes, drugs and as an accelerator in vulcanization of rubber [21]. Benzene is a non- polar solvent, which can freely miscible with many organic solvents [22]

Consequently, a study of the thermodynamic properties of ternary mixtures of acrylonitrile with benzene in aniline, N-methyl aniline and N-N-di methyl aniline is of considerable interest. Moreover, a

literature survey indicates that no ultra-sonic study on these ternary systems has been reported. Therefore, the present study was undertaken in order to have a deeper understanding of the intermolecular interactions between the components of the ternary liquid mixtures. For a better understanding of the physico-chemical properties and the molecular interactions between the participating components of these mixtures ultrasonic velocities and densities are measured at 303K, 308K and 313K over the entire concentration range for three ternary mixture systems.

II. MATERIALS AND METHODS

The chemicals used in the present work were analytic Reagent grade obtained from E-Merck, India. The mixtures of various concentrations in mole fraction were prepared by taking analytical reagents. In all the mixtures, the mole fraction of Benzene (X_2= 0.4) was kept fixed while the mole fractions of remaining Acrylonitrile with aniline were varied from 0.1 to 0.6 so as to have mixture of different concentration. The density was determined using a specific gravity bottle by relative measurement method. The weight of the sample was measured using an electronic digital balance. An Ostwald's viscometer (10 ml) was used for the viscosity measurement. An Ultrasonic Interferometer having a frequency of 2MHz (Mittal Enterprises, New Delhi, Model: F-81) has been used for velocity measurement. An electronically digital operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. Density and viscosity measurements were carried out in a well stirred water bath whose temperature was controlled to 0.01K.

III. THEORY AND CALCULATIONS

Using the measured data of density (ρ), velocity (U) and viscosity (η), the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) and Gibb's free energy (ΔG) have been calculated by the following standard expressions

Intermolecular free length

$$L_f = K_T \beta^{1/2} m$$

Where K_T is temperature dependent constant called as Jacobson constant and β is the adiabatic compressibility that can be calculated from the velocity of sound and the density of the medium.

$$\beta = \frac{1}{\rho U^2} \quad N^{-1}m^{2.}$$

The relation for free volume in terms of ultrasonic velocity and viscosity of the liquid

$$V_f = \left[\frac{M_{eff}\, U}{K\eta}\right]^{3/2} \quad M^3 mol^{-1}$$

The expression for the internal pressure by the use of free volume as

$$\pi_i = bRT\left[\frac{K\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M^{7/6}}\right] \quad Pa$$

Viscous Relaxation time (τ)

$$\tau = \frac{4}{3}\eta\beta$$

Acoustic impedance (Z)

$$Z = U\rho$$

IV. RESULTS AND DISCUSSION

The experimentally measured values of ultrasonic velocity, density and viscosity for the liquid mixtures of acrylonitrile (AN) with benzene in N-N- di methyl aniline at 303, 308 and 313K were listed in the Table I. The computed values of adiabatic Compressibility, free length and free volume for all the mixtures were depicted in Table II. Table III represents the calculated values of internal pressure and acoustic impedance respectively. Table IV depicts the computed values of relaxation time and absorption co efficient for the mixtures.

From the table I it was found that the density and viscosity decreases with increase in mole fraction of N-N di Methyl aniline (amine group) for all the system and decrease with increase in temperature. Viscosity decreases in system, suggesting thereby more association between solute and solvent molecules. Further sound speed increases with increase in mole fraction of amine group and increase with increase in temperature. This velocity behaviour is different from the ideal mixture and this can be attributed to the intermolecular interaction in the systems [23]. When benzene is added with aniline, dipole-induced dipole interaction arises between NH_2 and the loop of 6π electrons of benzene ring. Acrylonitrile is highly polar. The behaviour of their mixtures can be explained in term of 1) physical forces: dispersion, and 2) chemical forces: dipole-dipole interactions

TABLE I
Density (ρ), ultrasonic velocity (U),Viscosity at 303K, 308K and 313K

Mole fraction		Density x10^3 Kg/m^3			Viscosity (η) (10^{-3}Nsm^{-2})			Velocity (U) (ms-1)		
X1	X3	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.0999	0.5999	0.7555	0.7481	0.7471	0.3351	0.2164	0.1614	1560.2	1566	1574.2
0.1999	0.5000	0.7383	0.7349	0.7333	0.2889	0.1904	0.1447	1566.1	1570.2	1579.2
0.2999	0.4000	0.7376	0.7244	0.723	0.269	0.1746	0.133	1582.5	1583.8	1584.8
0.4000	0.3000	0.7218	0.7159	0.7142	0.2376	0.1553	0.1174	1584.4	1585.20	1586
0.5000	0.2000	0.7073	0.704	0.703	0.2138	0.1400	0.1056	1591.3	1594.00	1594.9
0.6000	0.0999	0.696	0.6896	0.6859	0.1919	0.1246	0.0934	1596.8	1597.2	1598.1

TABLE II
Adiabatic compressibility (β), free length and free volume at 303K, 308K and 313K

Mole fraction		β x 10^{-10} Pa^{-1}			L_f x 10^{-11} m			V_f x 10^{-13} m^3mol^{-1}		
X1	X3	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.0999	0.5999	5.4375	5.4507	5.4013	4.6527	4.6584	4.6372	13.7926	7.1976	4.6726
0.1999	0.5000	5.5224	5.5190	5.4682	4.6889	4.6874	4.6658	10.006	5.3745	3.5914
0.2999	0.4000	5.4136	5.5032	5.5069	4.6425	4.6807	4.6823	8.1637	4.2742	2.8443
0.4000	0.3000	5.5189	5.5587	5.5663	4.6874	4.7043	4.7075	6.0112	3.1789	2.0909
0.5000	0.2000	5.5833	5.5905	5.5921	4.7147	4.7177	4.7184	4.5296	2.4063	1.5776
0.6000	0.0999	5.6349	5.6843	5.7086	4.7364	4.7571	4.7673	3.351	1.7538	1.1392

TABLE III
Internal Pressure (πi) and Acoustic impedance(Z) at 303K, 308K and 313K

Mole fraction		πi x 10^4 Pa			Z x10 ^{5}Nm^{-2}		
X1	X3	303K	308K	313K	303K	308K	313K
0.0999	0.5999	5.7610	4.6665	4.0812	11.7873	11.7152	11.7608
0.1999	0.5000	5.7011	4.6841	4.1319	11.5625	11.5393	11.5802
0.2999	0.4000	5.9673	4.8265	4.2739	11.6725	11.4730	11.4581
0.4000	0.3000	6.0730	4.9624	4.3766	11.4362	11.3484	11.3272
0.5000	0.2000	6.2803	5.1455	4.5358	11.2552	11.2217	11.2121
0.6000	0.0999	6.5751	5.3518	4.6906	11.1137	11.0142	10.9613

TABLE IV
Absorption Coefficient (α / f^2) and Relaxation Time (τ) at (303K, 308K, 313K)

Mole fraction		α / f^2 10^{-15} Nps^2m^{-1}			τ X10 $^{-13}$ s		
X1	X3	303K	308K	313K	303K	308K	313K
0.0999	0.5999	3.0706	1.98038	1.4560	2.4289	1.5723	1.16208
0.1999	0.5000	2.6784	1.7595	1.3173	2.1267	1.4007	1.05473
0.2999	0.4000	2.4195	1.5951	1.2151	1.9412	1.2808	.976325
0.4000	0.3000	2.1760	1.4318	1.0833	1.7479	1.1507	.871108
0.5000	0.2000	1.9723	1.2909	.97350	1.5912	1.0433	.787176
0.6000	0.0999	1.7805	1.1659	.87720	1.4414	.94413	.710736

From the table II it was observed that as the concentration increases, there was an decrease in adiabatic compressibility, free length and free volume. The adiabatic compressibility shows an inverse behaviour compare to the ultrasonic velocity in the mixtures with increase in concentration. It is primarily the compressibility that changes with the structure and this lead to the change in ultrasonic velocity. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes take place due to the existence of electrostatic field. The intermolecular free length and adiabatic compressibility supports the variation of sound speed in the system. Arise in temperature leads to less disordered structure and more spacing between the molecules. The decrease in density and viscosity with temperature indicates that decrease in intermolecular forces due to increase in thermal energy of the system [24].

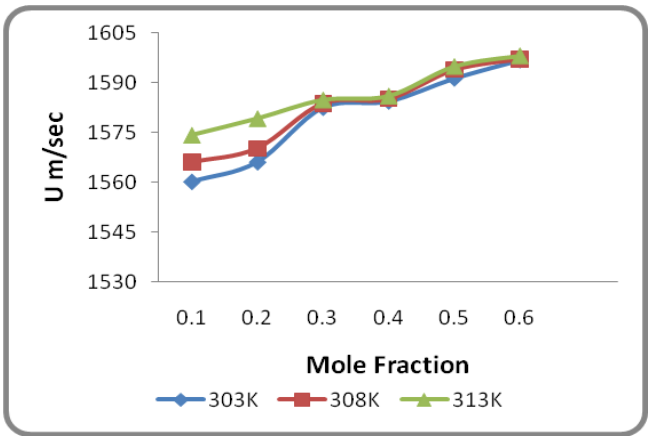

Fig. 1 Ultrasonic Velocity Vs Mole Fraction

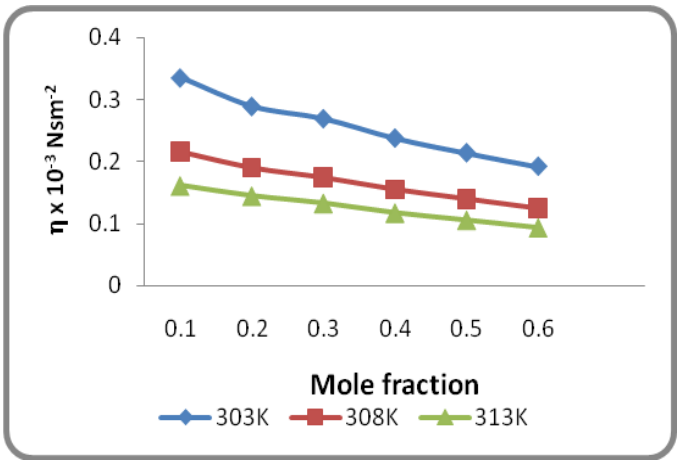

Fig. 2 Viscosity Vs Mole Fraction

The addition of aniline with the mixture of benzene disturbs the structure due to the presence of dipole-induced dipole interactions. This contributes to a decrease in free length and hence compressibility. The regular fall in free length with the mole fraction of aniline may be attributed to the close approach of the

molecules. According to Eyring and Kincaid [25] the regular fall in free length causes a rise in sound velocity in the mixture. This is also in accordance with expected decrease in adiabatic compressibility following an increase in the sound velocity in all the mixtures studied. Further this trend is an indication of clustering together of the molecules into some cage like agglomerates due to associative effect of the polar group predominating over the other types of interactions [26]. The former factor increases the intermolecular free length as described by Ja-cobson [26]

From table III The internal pressure may give information regarding the nature and strength of forces existing between the molecules [27]. In pure acrylonitrile there are dipole-dipole as well as the usual dispersive interactions. The effect of adding a non-polar second component is primarily to disrupt the dipolar inter-action of the first component, but if the second component is also polar, then dipole-dipole interactions between unlike molecule are most likely to occur which results in a volume contraction and the mixture becomes less compressible [28].

The free volume is the space available for the molecule to move in an imaginary unit cell. This reduces internal pressure. As stated above the internal pressure (πi) decreases with increase in concentration of Acrylonitrile in the systems. The decrease in free volume shows that the clustering is due to dipole-induced dipole interaction. It is primarily due to the formation of spherical cage-like structure owing to the closer packing of the molecule [29]

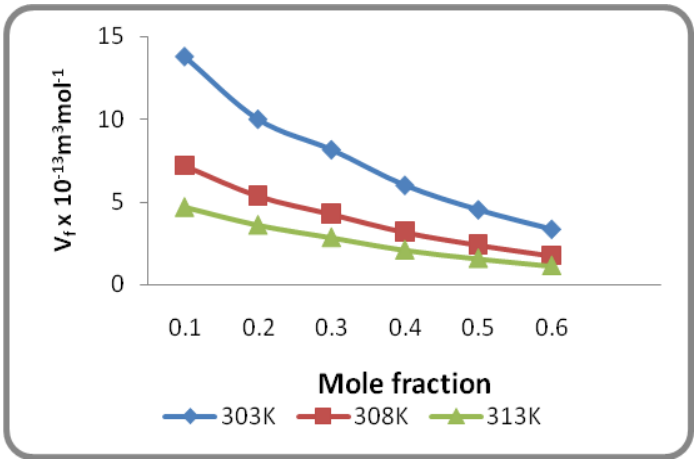

Fig. 3 Free Volume Vs Mole Fraction

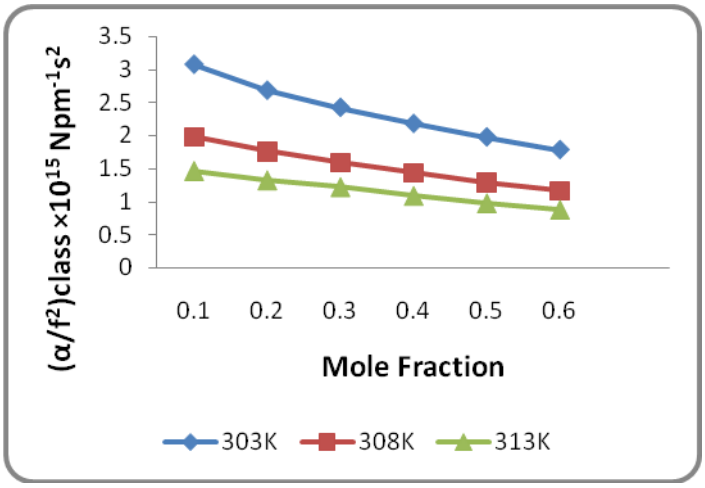

Fig. 4 Absorption Coefficient Vs Mole Fraction

The relaxation time decreases with increase in temperature. This suggest that the closed packing of molecules inside the shield. Similar results in some liquid mixtures were also reported by others [10]. The relaxation time (τ) increases with increase in mole fraction, which is in the order of 10^{-12} sec., is due to structural relaxation process [30] and in such a situation, it is suggested that, the molecule gets rearranged due to co-operative process [31]. Hence acrylonitrile forms stable complex with N,N- di methyl aniline Due to the electron releasing methyl groups in N,N– di methyl aniline [31].

V. CONCLUSION

The results obtained for the present study indicates that the molecular interaction is present in the liquid mixtures. From Ultrasonic velocity and its related acoustic parameters for ternary mixtures of acrylonitrile with benzene in N-N –di methyl aniline for various concentrations at 303K, 308K and 313K, The result establish that amine molecule forms donor-acceptor with Acrylonitrile in benzene. The formation constants indicate the presence of electron releasing group in acceptor molecules. The dipole induced dipole interaction is higher in acrylonitrile with benzene in– N N – di methyl aniline.

REFERENCES

[1] Eyring, H. & Kincaid, J. F. (1938). Free volumes and free angles ratios of molecules in Liquids. J. Chem. Phys.,6, 220–229.
[2] Mehta,S. K. & Chauhan,R. K. (1996).Ultrasonic velocity and apparent isentropic compressibility in mixtures of non-electrolytes J.Sol.Chem., 26, 295–308.
[3] Dewan, R. K., Gupta, C. M. & Mehta, S. K. (1988). Ultrasonic study of ethylbenzene + n- alkanols.Acoustica, 65, 245.
[4] Patil K J &Ali S I,Indian J Chem,22A(1983)410.
[5] RamchandranD,RambabuK,DevarajaluT&KrishnaiahA,JIndianChem Soc,73(1996)385.
[6] Reddy B R&Reddy D L,Indian J Pure &ApplPhys, 37 (1999)13.
[7] Rai R D ,Shukla,Shukla A K &Pandey J D,J ChemThermodyn, 21(1989)125.
[8] MehraR&Israni R, Indian J Pure &applPhys 38(2000)341.
[9] Mehra R Gupta A &Israni R, Indian J Pure &ApplPhys 40A(2001)505
[10] Pandey J D,Sharma A K ,PandeyA,Soni N K& Mukherjee S,Indian J Pure & Appl.Phys,39(2001)149..
[11] DeshmukhC,Dosh A G&Deshmukh C M,Indian J Pure Appl.Phys,48(2003)21
[12] Ali A,Nain A K,ChandD&LalB,Indian J Pure & Appl.Phys,41(2003)901.
[13] Mehra R &Pancholi M,J Pure &Appl Ultrason,27(2005)92.
[14] MehraR&PancholiM,Indian J Phys,80(2006)253
[15] Bedera G R, Bhandakkar V D and Suryavanshi B.M, International Symposium, Material Science and Engineering

[16] Edward I Peters; Introduction to chemical principles (ch/4), 3rdEdu CCBS college publishing (Philadelphia), 1982, 324.
[17] Aminabhavi, T.M., Banerjee, K.: Density, viscosity, refractive index, and speed of sound in binary mixtures of acrylonitrile with methyl acetate, ethyl acetate, N-propyl acetate, N-butyl acetate, and 3-methylbutyl-2-acetate in the temperature interval (298.15–308.15) K. J. Chem. Eng. Data 43, 514–518(1998)
[18] Haijun, W., Goukong, Z., Mingzhi, C.: Vapor-liquid equilibria of 1-propanol or 2- propanol with 2,2,4-trimethylpentane at 101 kPa.
[19] J. Chem. Eng. Data 26, 457–465 (1994)3.Sandhu, J.S., Singh, A.: Excess molar volumes of (acrylonitrile + an n-alkan-1-ol) at the temperature298.15 K. J. Chem. Thermodyn. 24, 81–84 (1992)
[20] Thermodynamic and Transport Properties of Aromatic Amine with Ketone in Nonpolar Solvent at 303.15, 308.15 and 313.15K N. S. Priya1, R. Kesavasamy2, R. Palani3 and M. Umadevi4Asian Journal of Applied Sciences (ISSN: 2321 0893) Volume 02 Issue 05, October 2014
[21] Molecular Interaction Studies on Aniline Containing Organic Liquid Mixtures Using Ultrasonic Technique P. Vasantharani, L. Balu, R. EzhilPavai and S. Shailajha Global Journal of Molecular Sciences 4 (1): 42-48, 2009)
[22] Jain, R.P., 1994. Text book of Engineering Chemistry, Sultan Chand and Sons., New Delhi
[23] Molecular Interaction Studies on Aniline Containing Organic Liquid Mixtures Using Ultrasonic Technique P. Vasantharani, L. Balu, R. EzhilPavai and S. Shailajha Global Journal of Molecular Sciences 4 (1): 42-48, 2009)
[24] AN. Kannappan, R. Kesavasamy and V. Ponnuswamy (MOLECULAR INTERACTION STUDIES OF H-BONDED COMPLEXES OF BENZAMIDE IN 1-4 DIOXAN WITH ALCOHOLS FROM ACOUSTIC AND THERMODYNAMIC PARAMETERS American J. of Engineering and Applied Sciences 1 (2): 95-99, 2008 ISSN 1941-7020 © 2008 Science Publications
[25] Erying, H. And J.F. Kincaid, 1938. Free volumes and free angle ratio of molecules in liquids. J. Chem Phys., 6: 620-629
[26] N.S.Priya1, RKesavasamy2,R.Palani3andM.UmadeviThermodynamic and Transport Properties of Aromatic Amine with Ketone in Nonpolar Solventat 303.15, 308.15 and 313.15KAsian Journal of Applied Sciences (ISSN: 2321 –0893)Volume 02–Issue 05, October 2014
[26] Hemalatha, B., 2004. Acoustical behavior of ternary liquid systems and solids.Ph.D Thesis.Department of Physics.Annamalai University.
[27] Jacobson, B.: Intermolecular free lengths in the liquid state; adiabatic and isothermal compressibilities.Acta Chem. Scand. 6, 1485–1497 (1952)
[28] jacobson].Venkatesu, P., Rao, M.V.P.: Excess volumes of ternary mixtures of N,N -dimethylformamide + methylisobutyl ketone+1-alkanols at 303.15 K. Fluid Phase Equilib. 98, 173–178 (1994)
[29] Hilde Brand, J.H. and R.L. Scott, 1962.Regular solutions. Prentice Hall, USA
[30] Kinsler LE &Rray A R, Fundamental of Acoustic Wiley eastern, New Delhi,1989 .
[31] Hyder A & Nair A K, Indian journal of pureand applied Physics, 63,7413,2000
[32] S. Srinivasan,S. Chidambar Avinayagam &B. S. SanthiGJRA - GLOBAL JOURNAL FOR RESEARCH ANALYSISX 15Volume-3, Issue-8, August-2014 ISSN No 2277 - 8160Ultrasonic Studies on Molecular Interaction of Aniline, N-Methyl Aniline, N, N-Di methyl Aniline and Cinnamaldehydein N Hexane Solution at 303K