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Acoustical and thermodynamical properties of amides with benzonitrile at 303, 308 and 313K

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ABSTRACT

Density (ρ), viscosity (η) and ultrasonic velocity (U) have been carried out in three binary liquid mixtures of dimethylformamide (DMF), N-methylacetamide and N,N-dimethyl acetamide in benzonitrile at 303, 308 and 313K The experimental data have been used to calculate the adiabatic compressibility (β), free volume (V_f), Gibb's free energy (ΔG), Grunberg interaction parameter (d) and their excess values. The results of excess parameter can be discussed in the light of intermolecular interaction in the binary mixtures.

Key words: Adiabatic compressibility, free volume, interaction parameter.

INTRODUCTION

Ultrasonic investigations find extensive applications in characterizing aspects of physico-chemical behaviour of binary liquid mixtures[1,2]. Ultrasonic velocity measurement provides an important tool to study the liquid state. Such studies have been used to understand the intra and intermolecular interactions in pure liquids[3], aqueous solution[4], and binary mixtures[5]. Detailed information about the nature of molecular interactions can be obtained from various ultrasonic parameters computed on the basis of experimental investigations. Measurement of ultrasonic velocity and its related properties in liquid mixtures play an important role to study physico-chemical behaviour and also explain the nature of molecular interactions[6,7]. Samatha[8,9] have measured ultrasonic velocity in the mixtures of N,N-Dimethyl acetamide with phenols and found that the excess compressibility and excess volumes have the same sign. Hari Babu and Rama Krishna[10] investigated ultrasonic behaviour of aqueous solutions of N,N-dimethyl formamide and dimethyl sulphoxide and attributed the results to hydrogen bonded complex formation. Many investigators[11,13] have studied the propagation characteristics of ultrasonic waves in liquid mixtures and utilized the data to understand intermolecular interactions. The study of solution properties of liquid mixtures consisting of polar as well as non-polar components find applications in industrial and technological process. The investigations regarding the molecular association in organic binary mixtures having 1-alkanol group as one of the components is highly polar and can associate with any other group having some degree of polar attractions. Dimethylformamide (DMF), N-methyl acetamide (NMA), N,N-dimethyl acetamide (DMA) are important because of its utilization in a broad range of applications in medicine and industries. Dimethylformamide is an aprotic solvent with low evaporation rate. It is also used to production of acrylic fibers and plastics. Further, it is used to as a solvent in peptide coupling for pharmaceuticals in the development and production of pesticides and in the manufacture of adhesives, synthetic leathers, fibers, films and surface coatings. In view of the important mentioned an attempt has

been made to elucidate the molecular interactions of dimethylformamide, N-methylacetamide and N,N-dimethyl acetamide with benzonitrile at 303, 308 and 313K through ultrasonic velocity measurement. Further the excess values of some of the acoustical and thermodynamical parameters have been calculated from the measurements of ultrasonic velocity, density and viscosity of the mixtures. The excess functions are used to explain intermolecular interactions in their binary mixtures.

MATERIAL AND METHODS

All the chemicals used in the present research work are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merck, Germany and SdFine chemicals, India, which are used as such without further purification. The purities of the above chemicals were checked by density determination at 303, 308 and 313K ± 0.1K which showed an accuracy of ± 1 × 10^{-4} gcm^{-3} with the reported values[14,15]. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density, viscosity and ultrasonic velocity were measured as a function of composition of the binary liquid mixture of benzonitrile with an amide at 303, 308 and 313K. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 $kg{\times}m^{-3}$. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200). An Ostwald's viscometer (10ml) was used for the viscosity measurement and the efflux time was determined using a digital chronometer to within ±0.01s. An ultrasonic interferometer having the frequency of 3 MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of ± 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with an accuracy of ± 0.1 K.

Theory and calculations

Various physical and thermodynamical parameters are calculated from the measured data such as

Adiabatic Compressibility $$\beta = \frac{1}{U^2\rho} \quad ...(1)$$

Free volume $$V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{3/2} \quad ...(2)$$

where M_{eff} is the effective molecular weight (M_{eff} =S$m_i x_i$, in which m_i and x_i are the molecular weight and the molefraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28 × 10^9 for all liquids.

The Gibb's free energy can be estimated from the following relation.

$$\Delta G = KT \ln\left(\frac{KT\tau}{h}\right) \quad ...(3)$$

where K is the Boltzmaan's constant (1.23 × 10^{-23} JK^{-1}), T the absolute temperature, 'h' the Planck's constant and t is the relaxation time

$$\left(\tau = \frac{4}{3}\eta\beta\right)$$

Excess values of the above parameters can be determined using

$$A^E = A_{exp} - A_{id} \quad ...(4)$$

where $A_{id} = \sum A_i X_i$ is any acoustical parameters and X_i the molefraction of the liquid component.

Grunberg[16] and Nissan formulated the following relation between the viscosity of a binary liquid mixture and pure components.

$$\ln \eta_{mix} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1X_2d \quad ...(5)$$

where d is an interaction parameter regarded as a measure of the strength of molecular interactions between the mixing components.

RESULTS AND DISCUSSION

The experimental values of density, viscosity and ultrasonic velocity for pure liquids and three binary liquid systems at 303, 308 and 313K

are given in Table.1. The excess values of viscosity (η), adiabatic compressibility (b), free volume (V_f), Gibb's free energy (ΔG) and Grunberg interaction parameter (d) are also presented in Tables.2-3. The variation of excess parameters with the molefraction of amides (X_2) in benzonitrile at different temperatures are plotted in Figs. 1-4 and the curves are drawn using least square fitting.

The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixture. The sign and extent of deviation of excess parameters depend on the strength of interaction between unlike molecules. The measurement of viscosity in binary mixtures yields some reliable information in the study of molecular interaction. According to Fort *et.al.,*[17] the excess viscosity gives the strength of the molecular interaction between the interacting molecules. For systems, where dispersion, induction and dipolar forces which are operated by the values of excess viscosity are found to be negative, where as the existence of specific interactions leading to the formation of complexes in liquid mixtures tend to make excess viscosity positive. The excess viscosity (Fig.1) is positive in systems I and except 0.1 molefraction of III, but it found to negative in system II. However these values are decreases with rising of temperature. The observed behaviour of positive excess viscosity in DMF and DMA with benzonitrile mixtures suggests the existence of specific interaction than NMA system. The decreasing behaviour of η^E with rising temperature suggests the weakening of interactions.

Table 1: Values of density (ρ) viscosity (η) and ultrasonic velocity (U) for

Molefraction (X_2)	ρ/ (kg m^{-3})			η/(×10^{-3} Nsm^{-2})			U/(m.s^{-1})		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
System-I: benzonitrile (x_1) + dimethylformamide (x_2)									
0.0	995.8	990.9	988.1	1.1186	1.0632	0.9828	1401.6	1400.4	1398.7
0.1	985.7	984.9	981.9	1.3272	1.2417	1.1301	1378.2	1393.2	1402.2
0.3	979.2	976.3	974.3	1.2569	1.1282	0.9655	1386.0	1400.4	1413.6
0.5	969.5	967.8	963.9	1.2319	1.0570	0.9499	1398.0	1402.8	1424.4
0.7	957.1	956.5	951.1	1.0763	1.0173	0.8673	1404.5	1405.2	1430.2
0.9	944.3	941.9	938.3	0.8762	0.8642	0.7806	1421.4	1440.6	1477.5
1.0	938.7	935.2	928.7	0.7626	0.7172	0.6768	1486.2	1464.2	1447.2
System-II: benzonitrile (x_1) + N-methylacetamide (x_2)									
0.0	995.8	990.9	988.1	1.1186	1.0632	0.9828	1401.6	1400.4	1398.7
0.1	997.9	997.5	993.4	1.3317	1.0356	0.8204	1338.8	1393.2	1393.8
0.3	992.8	987.9	988.8	1.5692	1.2467	1.0091	1341.6	1398.2	1400.8
0.5	1058.6	1058.0	1053.6	1.8082	1.4375	1.0470	1343.0	1400.2	1402.2
0.7	1051.1	1050.0	1048.8	2.5482	1.9803	1.4596	1351.8	1403.7	1410.3
0.9	1039.4	1034.7	1034.1	4.1344	3.0735	2.1655	1355.7	1412.4	1452.3
1.0	949.6	946.8	941.5	4.1408	3.6648	3.1024	1363.8	1347.6	1327.8
System-III: benzonitrile (x_1) + N,N-dimethylacetamide (x_2)									
0.0	995.8	990.9	988.1	1.1186	1.0632	0.9828	1401.6	1400.4	1398.7
0.1	944.1	936.1	931.8	1.0816	1.0325	0.8656	1404.9	1408.2	1410.6
0.3	952.3	949.4	944.5	1.1231	1.0403	0.9588	1414.5	1424.0	1428.6
0.5	965.6	964.2	957.7	1.1736	1.0766	1.0145	1417.8	1427.8	1432.3
0.7	976.1	973.4	969.9	1.2271	1.1104	1.0899	1431.6	1436.9	1442.7
0.9	988.9	985.7	981.3	1.4721	1.3496	1.2129	1446.5	1450.6	1453.2
1.0	931.8	926.6	923.7	1.0502	0.9751	0.9085	1435.2	1430.4	1425.3

The Figs.2 show that the variation of excess adiabatic compressibility are negative in systems II and III (except 0.1 and 0.3 molefraction of X_2), but it found to be positive in system I. However, these values are increases with increasing the molefraction of X_2 in system I, but whereas it decreases in systems II and III as well as with rising of temperature. Fort *et.al.,*[17] found that the negative value of excess adiabatic compressibilities indicated greater interaction between the components of the mixtures. Positive values in excess properties correspond mainly to the existence of dispersive forces. The negative value of β^E is associated with structure forming tendency while a positive value is taken to indicate a structure-breaking tendency due to hetero-molecular interaction between the component molecules of the mixtures. In the present investigation the negative β^E values for ternary mixtures of systems II and III may be attributed to the formation of hydrogen bond between strong proton-aceptor group (C = O) and proton-donor group ($-NH_2/-NH$) in their molecules. The decreasing behaviour of β^E with rising of temperature reveals that less strengthening of interaction between benzonitrile and amide molecules.

Fig. 3 gives a qualitative picture of excess free volume for the studied binary liquid mixtures and these values are found to be negative in all systems studied. However, these values are decreases with increasing the molefraction of X_2 and it increases with rising of temperature in all the three systems studied. For some binary liquid mixture, Fort *et.al.,*[17] noticed the negative excess free volume tends to decrease as the strength of the interaction between the unlike molecules increases although they do not parallel with the excess compressibilities. The results of V_f^E is the resultant of contributions from structural opposing effects[18]. These may be divided arbitrarily into three types, namely, chemical, physical, and structural contributions. Physical contributions, which are non-specific interactions between the real species present in the mixture, contribute a positive terms to V_f^E. The chemical or specific intermolecular interactions result in a volume decrease, and these include charge-transfer type forces and other

Table 2: Excess values of viscosity (η^E), adiabatic compressibility (β^E) and free volume (V^E_F), for

Molefraction	η^E ($\times 10^{-3}$ Nsm^{-1})			β^E ($\times 10^{-10}$ m^2 N^{-1})			V^E_f ($\times 10^{-8}$m^{3}mol^{-1})		
(X_2)	303K	308K	313K	303K	308K	313K	303K	308K	313K
System-I: benzonitrile (x_1) + dimethylformamide (x_2)									
0.1	0.2442	0.2131	0.1779	0.2587	0.1008	0.0099	-4.87	-7.94	-3.72
0.3	0.2451	0.1688	0.0745	0.2916	0.1244	0.0374	-5.43	-6.94	-1.69
0.5	0.2912	0.1668	0.1201	0.3105	0.1838	0.0465	-6.60	-6.75	-3.42
0.7	0.2069	0.1964	0.0987	0.3875	0.2593	0.0503	-5.89	-7.21	-3.38
0.9	0.0779	0.1124	0.0732	0.3899	0.1118	0.2622	-3.44	-4.53	-2.24
System-II: benzonitrile (x_1) + N-methylacetamide (x_2)									
0.1	-0.0890	-0.2874	-0.3743	0.7378	-0.0482	-0.0763	-3.66	-1.84	-7.70
0.3	-0.4558	-0.5967	-0.6095	0.3193	-0.1692	-0.2844	-3.86	-3.27	-1.63
0.5	-0.8211	-0.9261	-0.9954	-0.1498	0.6602	-0.7737	-2.98	-2.55	-3.96
0.7	-0.6854	-0.0904	-1.0064	-0.2905	-0.7820	-0.9767	-2.66	-2.53	-8.79
0.9	-0.2961	-0.3304	-0.7246	-0.3721	-0.9009	-1.3549	-1.45	-1.23	-4.34
System-III: benzonitrile (x_1) + N,N-dimethylacetamide (x_2)									
0.1	-0.0301	-0.0219	-0.1098	0.2444	0.2278	0.2055	-0.65	-2.62	-5.00
0.3	0.0251	0.0035	0.0017	0.1067	0.0092	0.0319	-0.45	-2.30	-1.27
0.5	0.0893	0.0057	0.0689	-0.0089	-0.1241	-0.1609	-1.72	-2.90	-0.96
0.7	0.1565	0.1089	0.1591	-0.1819	-0.2615	-0.3283	-2.71	-3.21	-3.19
0.9	0.4152	0.3657	0.2969	-0.3673	-0.4416	-0.4875	-5.67	-6.32	-5.7

complex- forming interactions. This effects contributes negative values to V_f^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume. In other words, structural contribution arising from the geometrical fitting (interstitially accommodated) of one component into the other due to the differences

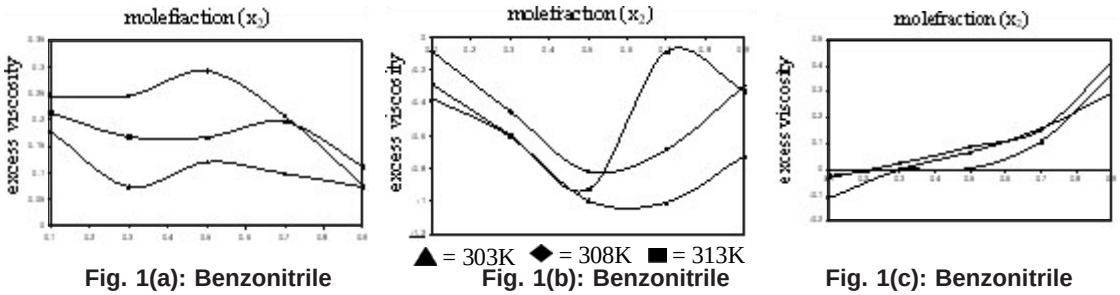

Fig. 1(a): Benzonitrile (x_1) + DMF (x_2) **Fig. 1(b): Benzonitrile (x_1) + NMA (x_2)** **Fig. 1(c): Benzonitrile (x_1) + DMA (x_2)**

Fig. 1: Variation of excess viscosity with molefraction of amides in benzonitrile at 303, 308 and 313K

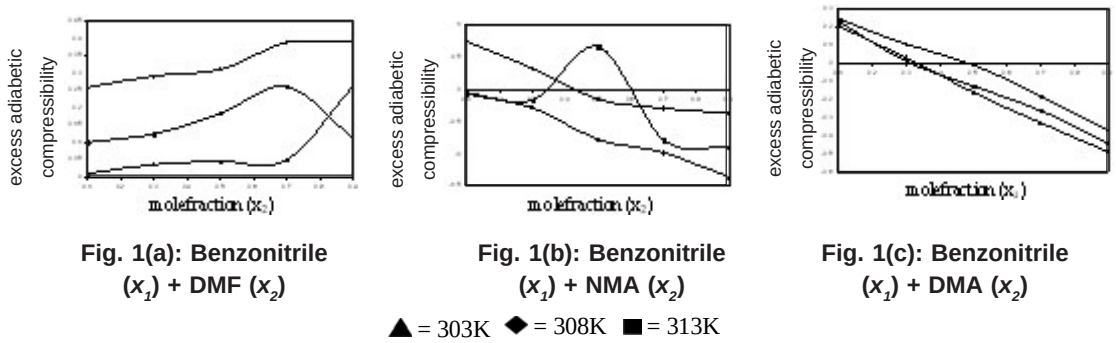

Fig. 1(a): Benzonitrile (x_1) + DMF (x_2) **Fig. 1(b): Benzonitrile (x_1) + NMA (x_2)** **Fig. 1(c): Benzonitrile (x_1) + DMA (x_2)**

Fig. 2: Variation of excess adiabatic compressibility with molefraction of amides in benzonitrile at 303, 308 and 313K

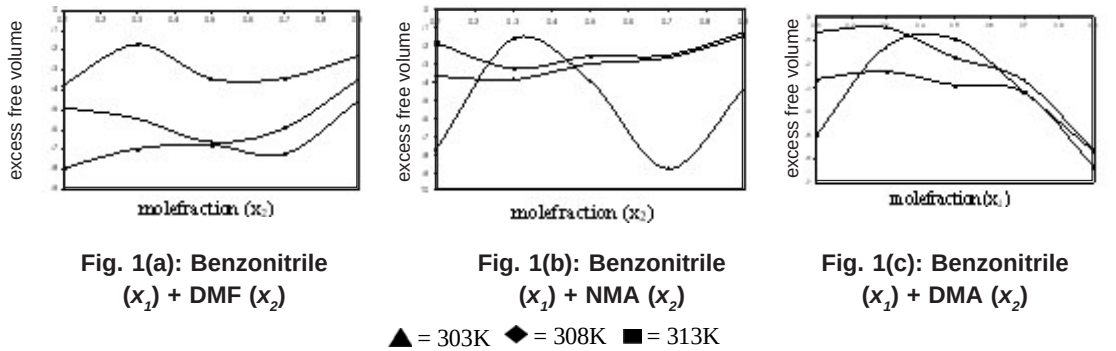

Fig. 1(a): Benzonitrile (x_1) + DMF (x_2) **Fig. 1(b): Benzonitrile (x_1) + NMA (x_2)** **Fig. 1(c): Benzonitrile (x_1) + DMA (x_2)**

Fig. 3: Variation of excess free volume with molefraction of amides in benzonitrile at 303, 308 and 313K

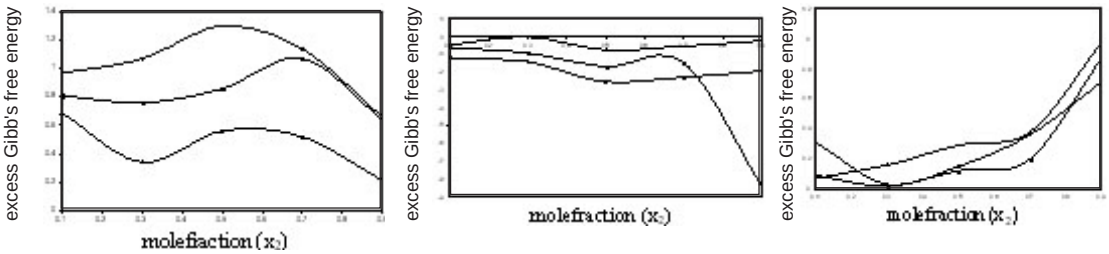

Fig. 1(a): Benzonitrile (x_1) + DMF (x_2) **Fig. 1(b): Benzonitrile (x_1) + NMA (x_2)** **Fig. 1(c): Benzonitrile (x_1) + DMA (x_2)**

▲ = 303K ◆ = 308K ■ = 313K

Fig. 4: Variation of excess Gibb's free with molefraction of amides in benzonitrile at 303, 308 and 313K

in the free volume and molar volume between components lead to negative contribution to V_f^E. Adgaonkar *et.al.,*[19] showed positive values of V_f^E, indicating the existence of weak molecular interaction in the liquid mixtures. However, in the present investigation the observed negative behaviour of V_f^E in all systems shows greater specific interaction. The increasing behaviour of V_f^E with rising of temperature shows the weakening of interaction which may due to the breaking of H-bonds between unlike molecules leading to an expansion in volume.

The variation of excess Gibb's free energy (Fig.4) is found to be positive in systems I and III where as it found to be negative in system II. The

Table 3: Excess values of Gibb's free energy (ΔG^E) and interaction parameter (d) for

Molefraction	ΔG^E / ($\times 10^{-20}$ KJmol^{-1})			d		
(X2)	303K	308K	313K	303K	308K	313K
System-I: benzonitrile (x1) + dimethylformamide (x2)						
0.1	0.97	0.81	0.69	2.3255	2.1618	1.9661
0.3	1.07	0.76	0.34	1.1024	0.8449	0.4483
0.5	1.30	0.86	0.56	1.1520	0.7639	0.6099
0.7	1.14	1.07	0.52	1.0933	1.1021	0.6481
0.9	0.66	0.64	0.21	0.9640	1.6342	1.1709
System-II: benzonitrile (x1) + N-methylacetamide (x2)						
0.1	-0.46	-0.60	-1.19	-2.4835	-1.6669	-3.2839
0.3	-0.02	-0.92	-1.42	-0.2576	-1.0094	-1.5153
0.5	-0.75	-1.68	-2.53	-0.6962	-1.2681	-2.0456
0.7	-0.54	-1.49	-2.28	-0.4415	-1.1625	-1.9479
0.9	-0.23	-8.39	-1.93	-1.4379	-0.5779	-2.7162
System-III: benzonitrile (x1) + N,N-dimethylacetamide (x2)						
0.1	0.07	0.09	0.31	0.3038	0.2294	1.3235
0.3	0.16	0.02	0.03	0.1095	0.0199	5.4281
0.5	0.29	0.12	0.15	0.3186	0.2231	0.2842
0.7	0.38	0.20	0.36	0.6518	0.4951	0.7546
0.9	0.97	0.87	0.71	3.6841	3.5152	3.1235

values of ΔG^E are increases with increasing the content of X_2 in systems I and III but it found to be decreases in system II as well as with rising of temperature. The positive deviation in ΔG^E may be attributed to specific interactions like hydrogen bonding and charge transfer, whereas the negative deviations may be ascribed to the dominance of dispersion forces. In the present investigation it is found that the observed behaviour of ΔG^E in system-I and III suggests the specific interaction than the other system. Recently, Ali[20] attributes the increasing positive values of ΔG^E in few binary liquid mixtures, to hydrogen bond formation between unlike molecules, which supports the present investigation. The magnitude of follows the sequence: DMA > DMF > NMA.

The interaction parameter 'd' in Grunberg and Nissan equation is a measure of the strength of interaction between the mixing compounds. d-values were said to indicate various types of interaction[21] as follows. Large and positive d-value indicated strong specific interaction; small positive value indicated weak specific interaction and large negative value indicated no specific interaction. It is evident from the Table.3 that d-value is positive in systems I and III and it found to be negative in system II. However these values are increases with increasing the content of X_2 in systems II and III, but it found to be decreases in system I as well as with rising of temperature. The positive values of 'd' in systems-I and III may be attributed to the dominance of specific interactions arising from the making of hydrogen bonds between nitrogen atom of —CN group of benzonitrile and hydrogen atoms of the amino group of amides. The magnitude of 'd' is in the order: DMA > DMF > NMA.

CONCLUSION

The excess ultrasonic properties reveal the existence of molecular interaction in the binary mixtures of benzonitrile with dimethylformamide (DMF), N-methyl acetamide (NMA) and N,N-dimethylacetamide (DMA) at 303, 308 and 313K. Strong molecular interaction through hydrogen bonding was observed between nitrogen atom of —CN group of benzonitrile and hydrogen atoms of the amino group of amides. From the magnitude of ΔG^E and Grunberg interaction parameter 'd', it can be concluded that the existence of molecular interaction in the mixture is in the order: DMA > DMF > NMA which depends upon the position of methyl groups in these amide molecules.

REFERENCES

1. Tamura, K. T. Sonoda, and S. Murakami, *J. Solution. Chem.,* **28**: 777 (1999).
2. Subrahmanyam Naidu, P and K. Ravindra Prasad, "Ultrasonic study in the binary liquid mixtures of dimethyl sulphoxide", *J. Pure & Appl. Ultrason.,* **24**: 18-23 (2002).
3. Anwar Ali and A.K. Nain, "Study of intermolecular interactions in binary mixtures of formamide with 2-propanol, 1,2-propanediol and 1,2,3-propanetriol through ultrasonic speed meaurements", *Ind. J. Pure & Appl. Phys.,* **39**: 421-427 (2001).
4. Ragoramane and Srinivasa Rao, "Ultrasonic velocity suties on the influence of electrolytes on molecular interactions in aqueous solutions of ethylene glycol", *Ind. J. Pure & Appl. Phys.,* **36**: 777-780 (1998).
5. Subrahmanyam Naidu, P and K. Ravindra Prasad, "Molecular interactions in the binary liquid mixtures", *Ind. J. Pure & Appl. Phy.,* **40**: 264-271 (2002).
6. Venkatesu, P., Pure Appl. Ultrasonics, **18**:15 (1996).
7. Subha, M.C.S., *Acustica Acta, Acustica*, 84 (1998).
8. Samatha, K., *Acoustica Acta. Acustica,* 82 (1998).
9. Samatha, K., *Pure Appl. Ultrasonics*, **20**: 1 (1998).
10. Haribabu, V.V., G. Ramakrishna Raju, K, Samata and J. Sreeramamurthy, *Ind. J. Pure & Appl. Phys*. **34**: 768 (1996).

11. Amalendu Pal and Rekha Gaba, "Volumetric, acoustic and viscometric studies of molecualr interactions in binary mixtures of dipropylene glycol, dimethyl ether with 1-alkanols at 298.15K", *J. Chem. Thermodyn.,* **40**: 818-828 (2008).
12. Amalendu Pal and Harsh Kumar, "Thermodynamic parameters of binary mixtures of some n-alkoxyethanols and polyethers with 1-propanol at 298.15K deduced from ultrasonic speed and viscosity data", *J. Pure & Appl. Ultrason.,* **26**: 67-79 (2004).
13. Anwar Ali, A. Yasmin and A.K. Nain, "Study of intermolecular interactions in binary liquid mixtures through ultrasonic speed measurements", *Ind. J. Pure & Appl. Phy.,* **40**: 315-322 (2002).
14. Dean Langues, J.A., *Hand Book of Chemistry* 12th Edn., McGraw-Hill, New York, (1979).
15. David, R.L., *Hand Book of Chemistry and Physics*, 72nd Edn., [CRC Press, Beston], (1992).
16. Grunberg, A.H., "*The viscosity of regular solutions, systems involving carbon tetrachloride, benzene and cyclohexane", Trans. Faraday. Soc,* **50**: 1293-1303 (1954)
17. Fort, R.J. and W.R. Moore, "Adiabatic compressibilities in binary liquid mixtures", *Trans. Farad. Soc.*, **61**: 2102-2110 (1965).
18. Treszczanowicz, A.J., O. Kiyohara, and G.C. Benson, "Excess volumes of n-alkanols + n-alkanes IV. Bianry mixtures of decan-1-ol + n-pentane, + n-hexane, + n-octane, + n-decane, and + n-hexadecane", *J. Chem. Thermodyn.,* **13**: 253-260 (1981).
19. Adgonokar, C.S. and P.K. Agnikotri, "Theoretical evaluation of ultrasonic velocity in binary liquid mixtures", *Ultrason,* **27**: 248-251 (1989).
20. Ali, A, Acoustics Letters **79**: 89 (1999).
21. Syamala, V., K. Sivakumar and P.J. Venkateswarlu, "Volumetric, ultrasonic and viscometric studies of binary mixtures of DMSO with chloro and nitro substituted aromatic hydrocarbons at T = 303.15K", *J. Chem. Thermodyn.,* **38**: 1553-1562 (2006).