



# VISCOSITY, DENSITY AND ULTRASONIC VELOCITY STUDIES OF BINARY AQUEOUS SOLUTIONS CONTAINING AMIDES

S.R. Patil<sup>a</sup>, P.P.Patil<sup>b</sup> and A. P. Manake<sup>c</sup> and R.D.Pawar<sup>d</sup>

<sup>a</sup>Department of Chemistry, MGSM's ASC College, Chopda. Maharashtra, India.(srpatil\_001@rediffmail.com)

<sup>b</sup>School of Chemical Sciences, North Maharashtra University, Jalgaon.

<sup>c</sup>Department of Chemistry, Pratap College, Amalner. Dist-Jalgaon. Maharashtra. Pin-425401, India.(apmanake@gmail.com)

<sup>d</sup>Department of Chemistry,A.C.S. College ,Yawal,M.S., India.

## ABSTRACT

Viscosity ( $\eta$ ), Density ( $\rho$ ) and Ultrasonic velocities (U) are reported for binary mixtures of N-Methylacetamide and N,N-Dimethylacetamide in aqueous medium have been measured and data is reported over entire range of mole fractions at 298.15K and atmospheric pressure. From the experimental data obtained the parameters like viscosity deviation ( $\Delta\eta$ ), Excess molar volume (VE), deviation in isentropic compressibility ( $\Delta K_s$ ) and excess properties like excess intermolecular free length (L<sub>fE</sub>), excess available volume (VaE) have been calculated.. It has been observed that, Substitution of H by -CH<sub>3</sub> at the N caused a noticeable effect on the VE values, as well as addition of DMF to solvent water causes dissociation of hydrogen bonding in the associated water molecules. The considerable changes have been observed for all the measured parameters and their changes well correlates to each other.

**Keywords:** Viscosity, Density, Ultrasonic velocities.

## 1. Introduction

The Viscosity ( $\eta$ ), Density ( $\rho$ ) and Ultrasonic velocities (U) measurements found wide applications in characterizing the physico-chemical behavior of liquid mixtures<sup>1-3</sup> and in the study of molecular interactions. Ultrasonic velocity of a liquid is related to the binding forces between the atoms or the molecules. Ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids<sup>4</sup> and

binary mixtures. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters and their excess -values with composition gives an insight into the molecular process<sup>5-7</sup>. The investigations regarding the molecular association in organic binary mixtures having amide group as one of the components is of particular interest, since amide group is highly polar and has large dipole moment<sup>8</sup> can associate with any other group having some degree of polar attractions. Water is protic solvent and is strongly associated due to highly polar O-H bonds. However, no thermodynamic studies have been conducted for binary mixtures of N-Methylacetamide and N,N-Dimethylacetamide, in aqueous medium. Hence experimental studies were carried out by the authors to characterize different amides through measurements of Viscosity ( $\eta$ ), Density ( $\rho$ ) and Ultrasonic velocities (U) at 298.15K. The main purpose of this study is to characterize the molecular interactions in these systems and subsequently to determine the effect of the substituent length of amides.

In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of amides aqueous medium at 298.15K. Further, the excess values of some of the acoustical ultrasonic velocity, density and viscosity of the mixtures. The excess functions are used to explain intermolecular interactions in these binary mixtures.

**2. Experimental**

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 Sd Fine chemicals, India, which are used as such without further purification. The purities of the above chemicals were checked by density determination at 298.15 K the uncertainty is less than ± 1x10<sup>-4</sup> gcm<sup>-3</sup>. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density, viscosity and velocity were measured as a function of composition of the binary liquid mixture of Distilled water with N-Methylacetamide and N,N-Dimethylacetamide respectively at 298.15K.

The density was determined using a Bi-capillary pycnometer. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.01 mg (Model: Shimadzu AX-200). An Ubbelohde viscometer (20ml) was used for the viscosity measurement and efflux time was determined using a digital clock to within ±0.01s. An ultrasonic interferometer having the frequency of 2 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 ± 0.01 K.

**3. Theory and Calculations**

Excess volumes are determined by,

$$V^E = \frac{M_1X_1 + M_2X_2}{\rho_{12}} - \frac{M_1X_1}{\rho_1} - \frac{M_2X_2}{\rho_2} \quad (1)$$

Viscosity of Binary Mixtures is determined by,

$$\ln \eta_m = X_1 \ln \eta_1 + X_2 \ln \eta_2 \quad (2)$$

Deviation in Viscosity of Binary Mixtures is determined by,

$$\Delta \eta_m = \eta_{12} - X_1 \eta_1 - X_2 \eta_2 \quad (3)$$

Deviation in isentropic compressibility have been evaluated by using the equation

$$\Delta k_S = k_S - \Phi_1 k_{S1} - \Phi_2 k_{S2} \quad (4)$$

Where  $k_{S1}$ ,  $k_{S2}$  and  $k_S$  are isentropic compressibility of liquid mixtures and  $\Phi$  is volume fraction of pure components.

The excess properties  $y^E$  are fitted by the method of non linear least squares to a Redlich kister type polynomial (eq. 5)

$$y^E = X_1 X_2 \sum A_i (X_1 - X_2)^i \quad (5)$$

In each case the optimum number of coefficients  $A_i$  was determined from an examination of the variation of standard deviation as calculated by,

$$\sigma y^E = X_1 X_2 [ \sum (y^E_{obs} - y^E_{calc})^2 / (n - m) ]^{1/2} \quad (6)$$

Where n represents the number of experimental points and m represents the number of coefficients in fitting the data.

$$L_f^E = L_{f_{mix}} - X_1 L_{f_1} - X_2 L_{f_2} \quad (7)$$

Excess values of the above parameters can be determined using

$$A^E = A_{exp} - A_{id} \quad (8)$$

Where  $A_{id} = \sum A_i X_i$ ,  $A_i$  is any acoustical parameters and  $X_i$  the mole fraction of the liquid component.

$$\text{Available volume } V_a = VT(1 - \frac{U}{V}) \quad (9)$$

Where U is the limiting velocity and is taken as 1600 ms and V is the molar volume at TK.

For binary liquid mixtures the equation for internal pressure can be written as

$$\Pi_{i12} = bRT (\frac{K_{\eta_{12}}}{U_{12}}) / M_{12}^{7/6} \quad (10)$$

$M_{12}$  is given by ,

$$M_{12} = X_1 M_1 + X_2 M_2 \quad (11)$$

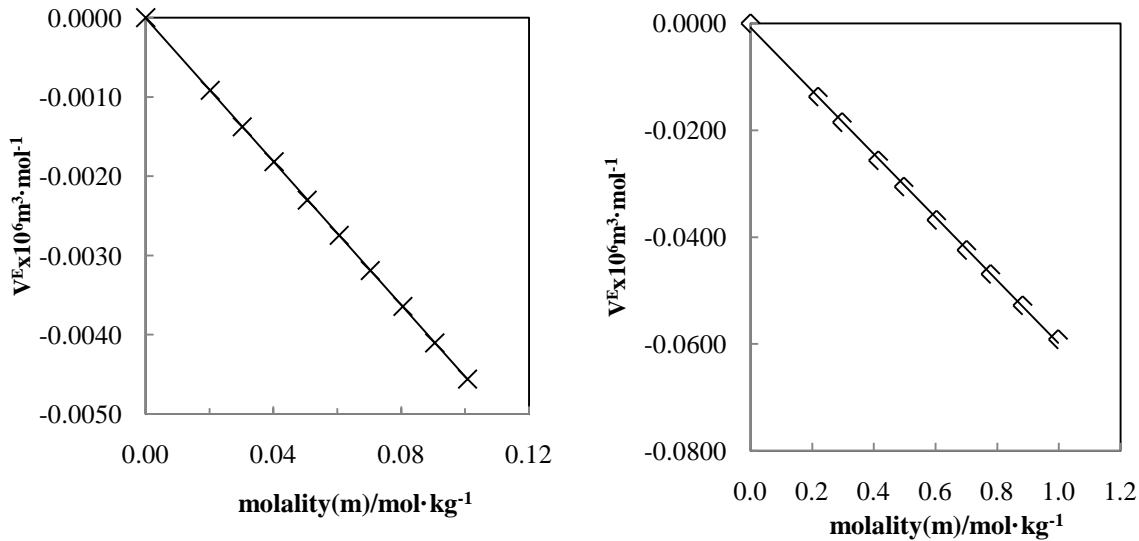
**Table 1- Densities, Viscosities, Excess molar volumes and Deviations in Viscosities for Amides+Water Binary systems at 298.15K.**

Mole fraction $x_1$	Molality m	Density P	$\eta$	$V^E$	$\Delta \eta$
<b>N-methylacetamide +Water</b>					
0.0000	0.0000	0.997043	0.89020	0.0000	0.000
0.0004	0.0202	0.997032	0.89426	-0.0009	0.285
0.0005	0.0302	0.997027	0.89627	-0.0014	0.427
0.0007	0.0402	0.997021	0.89827	-0.0018	0.567
0.0009	0.0506	0.997016	0.90036	-0.0023	0.714

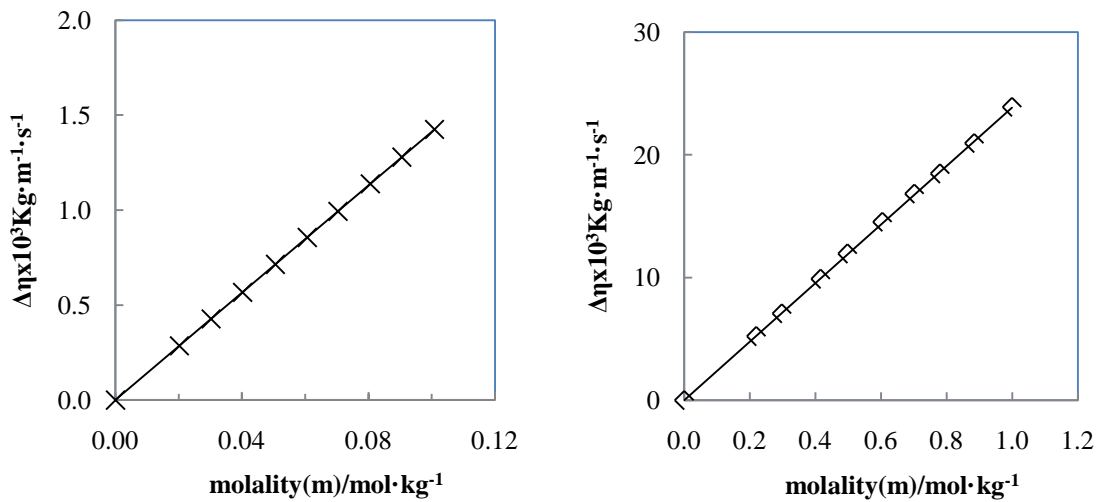
0.0011	0.0606	0.997010	0.90238	-0.0027	0.856
0.0013	0.0703	0.997005	0.90434	-0.0032	0.994
0.0014	0.0805	0.996999	0.90639	-0.0036	1.138
0.0016	0.0905	0.996994	0.90839	-0.0041	1.279
0.0018	0.1008	0.996988	0.91046	-0.0046	1.425
1.0000	0.0000	0.957000	4.20860	0.0000	0.000
<b>N,N-Dimethylacetamide +Water</b>					
0.0000	0.0000	0.997043	0.89020	0.0000	0.000
0.0039	0.2189	0.996581	0.94243	-0.0137	5.202
0.0053	0.2970	0.996417	0.96111	-0.0185	7.063
0.0074	0.4148	0.996168	0.98928	-0.0257	9.869
0.0089	0.4971	0.995995	1.00996	-0.0306	11.929
0.0108	0.6035	0.995770	1.03605	-0.0368	14.528
0.0125	0.7008	0.995565	1.05908	-0.0425	16.821
0.0138	0.7787	0.995401	1.07544	-0.0469	18.450
0.0157	0.8832	0.995180	1.10052	-0.0528	20.949
0.0177	0.9983	0.994938	1.13011	-0.0592	23.897
1.0000	0.0000	0.936390	0.94360	-0.0004	0.000

Table 2- Excess Parameters for Ultrasonic velocity for Amides(1)+Water at 298.15K.

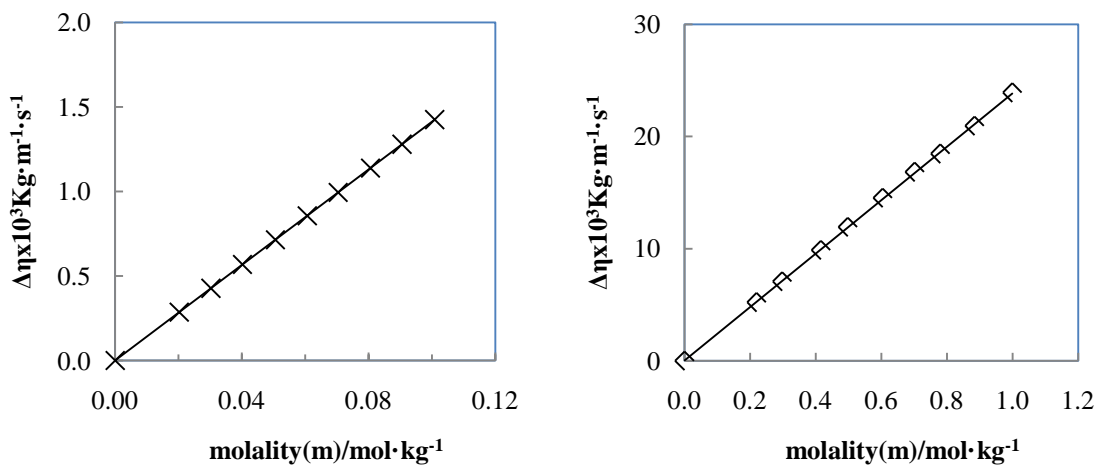
$x_1$	molality m	$\Phi$	$\Delta K_s$	$Z^E$	$L_f^E$	$Va^E$	$\Pi_{int}^E$	$H^E$
<b>N-methylacetamide+Water</b>								
0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
0.0011	0.0011	0.0011	0.0011	0.0011	0.0011	0.0011	0.0011	0.0011
0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014
0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018
<b>N,N-dimethylacetamide+Water</b>								
0.0039	0.0039	0.0039	0.0039	0.0039	0.0039	0.0039	0.0039	0.0039
0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
0.0074	0.0074	0.0074	0.0074	0.0074	0.0074	0.0074	0.0074	0.0074
0.0089	0.0089	0.0089	0.0089	0.0089	0.0089	0.0089	0.0089	0.0089
0.0108	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108
0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125
0.0138	0.0138	0.0138	0.0138	0.0138	0.0138	0.0138	0.0138	0.0138
0.0157	0.0157	0.0157	0.0157	0.0157	0.0157	0.0157	0.0157	0.0157
0.0177	0.0177	0.0177	0.0177	0.0177	0.0177	0.0177	0.0177	0.0177



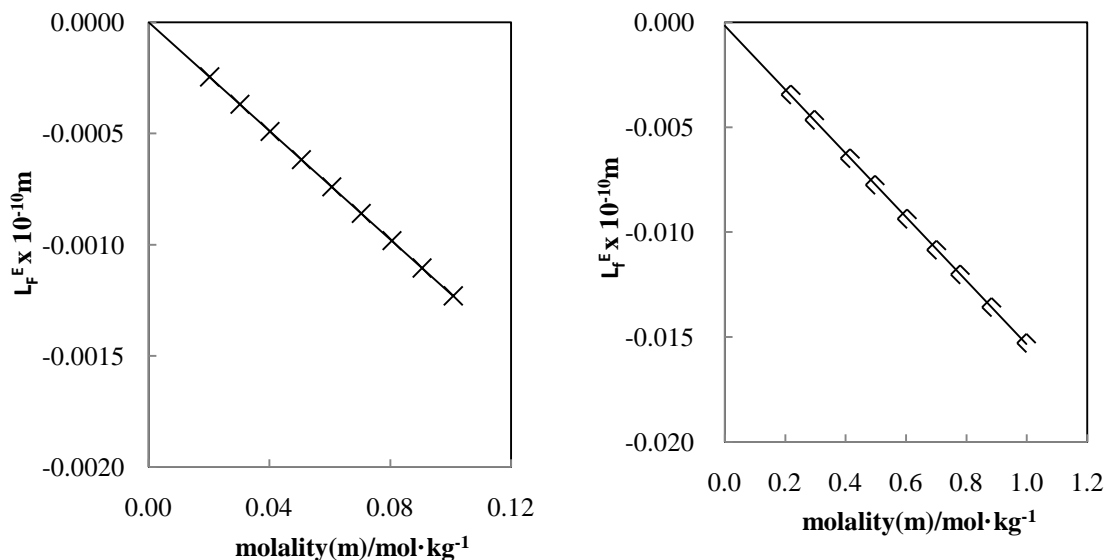
**Fig.-1: Variation of  $V^E$  as a function of molality (m) of amides in aqueous solutions (a): NMA(x);(b):DMA ( $\diamond$ ) at 298.15K.**



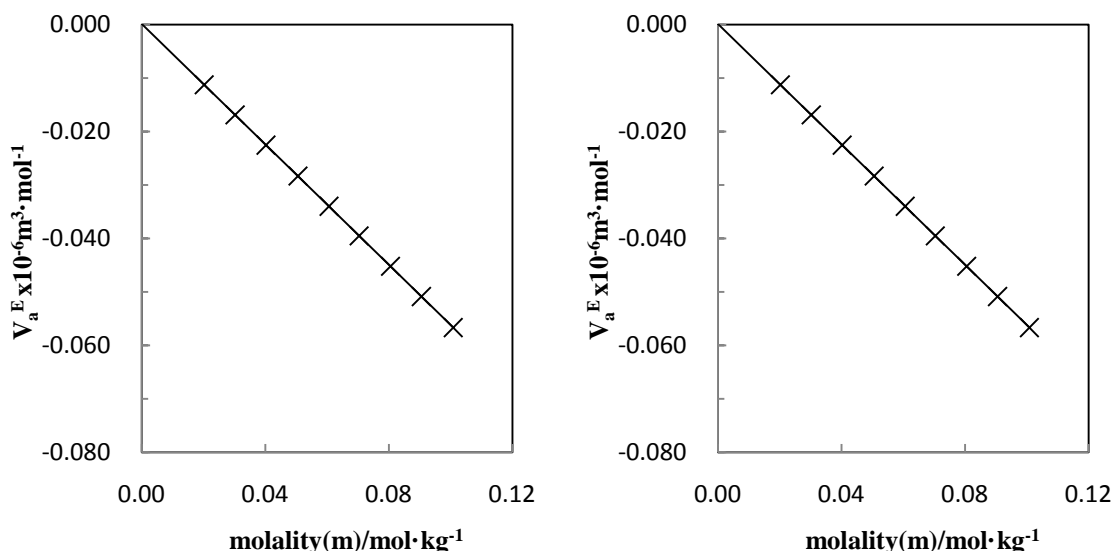
**Fig.-2: Variation of  $\Delta\eta$  as a function of molality (m) of amides in aqueous solutions (a): NMA (x); (b):DMA ( $\diamond$ ) at 298.15K.**



**Fig.-3: Variation of  $\Delta K_s$  as a function of molality (m) of amides in aqueous solutions (a): NMA (x); (b) :DMA ( $\diamond$ ) at 298.15K.**



**Fig.-4: Variation of  $L_F^E$  as a function of molality (m) of amides in aqueous solutions (a) :NMA (×) ; (b);DMA(◇) at 298.15K.**



**Fig.-5: Variation of  $V_a^E$  as a function of molality (m) of amides in aqueous solutions (a): NMA (×); (b): DMA (◇) at 298.15K.**

#### 4. Results and Discussion

In the pure state water has high degree of self association. This association decreases with increasing concentration of amides, when amides are mixed with water then there is interaction between their individual functional groups (H-O-H and -HN-C=O). The presence of electron withdrawing group in amides decreases its electron densities on oxygen atom in water. The polarity of water is less hence there degree of self-association is less as compared to amides<sup>9</sup> The experimental values

of density, viscosity and ultrasonic velocity, for the binary liquid systems at 298.15K, are given in Table 1 and 2. The values of excess volume ( $V^E$ ), viscosity deviations and ( $\Delta\eta$ ), deviation on isentropic compressibility ( $\Delta k_s$ ) for binary Systems of water and amides at 298.15 K. are presented in Tables-1 and 2 The variation of excess parameter with molality of amides ( $x_2$ ) at 298.15 K are plotted in Figures 1a and b to 5 a and b.

Fig:-1 a and b represents  $V^E$  values for N-Methylacetmide and N,N-

Dimethylacetamide respectively, which are negative over the entire concentration of the amides the values  $V^E$  parameter become more negative with increasing concentration of amides. This is because more association of amides with water molecules increases with increasing concentration of amides<sup>12</sup>. The observed  $V^E$  may be analyzed in terms of several effects, which may be divided into physical, chemical and geometrical contributions<sup>13</sup>. The physical interactions comprise mainly dispersion forces and non-specific physical interaction giving a positive contribution. The chemical interaction involves the charge transfer complexes, resulting in contraction of volume, geometrical or structural contribution arising from geometrical fitting of one component into other, due to difference in molar volume and free volumes between the components increases<sup>14</sup>. In the present investigation no positive deviations of  $V^E$  have been observed, attributed strong molecular interactions between the unlike molecules. The amides act as a lone pair donor for the formation of  $\text{NH}_4^+$  also amides form hydrogen bonding with water. The  $V^E$  parameter becomes more negative with increasing alkyl group on the N-atom this is due to increase in basicity of amides with increasing alkyl group.

Values of  $\Delta\eta$  are more negative at higher concentration of the amides (Fig. 2 a and b) provide additional evidence for the existence of strong interactions like dipole-dipole type between components of liquid mixtures<sup>11</sup>. According to Fort et. al. 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, the large positive values of excess viscosity for all the systems can be attributed to the presence of the dispersion, induction, and dipolar forces between the components. The magnitude of  $\Delta\eta$  is positive and shows linear increase with concentration of the amides indicates that the specific interactions leading to the formation of complexes in liquid mixtures tend to make  $\Delta\eta$  values positive.

It is seen from Fig. 3, 4 and 5 that the curves for  $\Delta k_s$ ,  $L_f^E$  and  $V_a^E$  values are negative over the entire concentration of the amides at 298.15K temperature these curves are linear with negative slope. The values of  $\Delta k_s$ ,  $L_f^E$  and

$V_a^E$  follows same order of interactions as that of  $V^E$ . N-Methylacetamide shows weakest while N,N-diethylacetamide shows strongest interactions. The negative  $\Delta k_s$ ,  $L_f^E$  and  $V_a^E$  may be attributed to the existence of dispersion and dipolar forces between unlike molecules and related to the difference in size and shape of the molecules<sup>10</sup>. Increase of concentration of the amides favors hetero and homo-association of the molecules which increases fluidity of the liquid.

## 5. Conclusion

Further, the small negative values of  $V^E$  and  $\Delta\eta$  for FA-Water system indicates a balance between dispersion forces and heteroassociation. Assorson and Eirich<sup>15</sup> suggested that two water molecules should interact with two lone pair of electrons on carbonyl oxygen while a third molecule is held more weakly on the sterically hindered lone pair of electrons of the disubstituted nitrogen. However, in N-Methylacetamide-water system hetero association is less reasonable and is less important than N,N-diethylacetamide solution.

The experimental data of Ultrasonic velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) are reported for binary mixtures of N-Methylacetamide and N,N-Dimethylacetamide over the entire range of mole fractions at 298.15K. Calculated viscosity deviation, excess  $V^E$ ,  $\Delta k_s$ ,  $L_f^E$  and  $V_a^E$  shows large negative deviations for all the investigated binary systems. This reveals the existence of molecular interactions in the binary mixtures. The present investigation shows that greater molecular interaction exists in dimethyl formamide-water mixture which may be due to strong hydrogen bond formation and more basicity and weak molecular interaction that exists in the formamide-water mixtures and which may be due to the dominance of dispersion forces and dipolar interaction between the unlike molecules.

## REFERENCES

- [1] Redlich, O., Kister, A. T. (1948). *Ind Eng Chem*, 40,345-348.
- [2] Oswal, S. L., Desai, H. S. (1998). *Fluid Phase Equilibria*, 149, 359-376.
- [3] Lei, Q., Hou, Y. (1999). *Fluid phase equilibria*, 154, 153-163.

- [4] Palani, R., Gutha, A., Saravanan, S., Tonatapure, S. D. (2008). *Rasayan J Chem*, 1,3,481-488.
- [5] Palani, R., Meenakshi, K. (2007). *Indian J Chem*, 46A, 252-257.
- [6] Patil, K. J., Mehta, G. R., Chandewar, R. K. (1986). *Indian J Chem*, 25A, 1147-1148.
- [7] Ali, A., Nain, A. K., Hyder, S. (1998). *J Indian Chem Soc*, 75, 501-505.
- [8] Shu-da, Chen., Lei, Qun-fang., Fang, Wen-jun. (2002). *J Chem Eng Data*, 47, 811-815.
- [9] Dzida, M. (2007). *J Chem Eng Data*, 52, 2, 521-532.
- [10] Pandharinath, S. N., Nikam, P. S., Mahale, T. R. (1996). *J Chem Eng Data*, 41, 2, 1055-1058.
- [11] Kapadi, U. R., Hundiware, D. G., Patil, N. B., Lande, M. K., Patil, N. B. (2001). *Fluid Phase Equilibria*, 192, 63-70.
- [12] Shu-da, Chen., Lei, Qun-fang., Wen-jun, Fang. (2005). *Fluid Phase Equilibria*, 234, 22-33.
- [13] Patil, S. R., Hiray, A. R., Deshpande, U. G. (2010). *Asian J Chem and Env Research*, 3, 2, 76-81.
- [14] Patil, S. R., Deshpande, U. G., Hiray, A. R. (2010). *Rasayan Journal of Chemistry*.
- [15] Assorson P., Eirich F. R. (1968). *J. Phys. Chem*, 72, p. 2710, 03, 166-73.