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

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ABSTRACT

Viscosity (η), Density (ρ) and Ultrasonic velocities (U) are reported for binary mixtures of Formamide (FA), N-Methylformamide (MFA) and N, N-Dimethylformamide (DMF) in an aqueous medium over an entire range of compositions at 298.15K and atmospheric pressure. From the experimental data obtained, viscosity deviation (Δη), deviation in isentropic compressibility (ΔKs) and excess properties like excess molar volume (V^E), excess intermolecular free length (L_f^E), excess available volume (V_a^E) and excess internal pressure (π_i^E) have been calculated and are fitted to Redlich-Kister type polynomial equation. The results obtained are interpreted in terms of molecular interactions among the studied amide solutions. The deviation from ideal mixing law in all calculated parameters are negative except deviation in viscosity and deviation in excess internal pressure for N-methylformamide and N,N-dimethylformamide-Water mixtures. This reveals the nature and magnitude of intermolecular interactions between unlike molecules and effect of $–CH_3$ in amides. Substitution of -H by $-CH_3$ at the N site caused a noticeable effect on the excess parameters.

Keywords: Viscosity, Density, Ultrasonic velocities, isentropic compressibility, excess free length, inter molecular interactions, Redlich–Kister polynomial equation.

INTRODUCTION

The Viscosity (η), Density (ρ) and Ultrasonic velocity (U) measurements find wide applications in characterizing the physicochemical behavior of liquid mixtures[1-3] and in the study of molecular interactions. From the direct measurement of density, mixing parameter like excess molar volume could interpret which provides valuable information about the nature and type of molecular interactions in binary organic liquid mixtures[4].Ultrasonic velocity and their related thermodynamic properties have been adequately employed in understanding the nature of molecular interactions in pure liquids[5] and binary mixtures. Studies on the molecular interactions from the knowledge of variation of thermodynamic parameters and their excess values with composition provide an insight to the molecular process[6-8]. 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 can associate with any other group having some degree of polar attractions as well as they also hold structural similarities to proteins[9]. Water is protic solvent and is strongly associated due to highly polar H-O bonds. However, no thermodynamic studies have been conducted for binary mixtures of Formamide (FA), N-methylformamide (MFA) and N,N-dimethylformamide (DMF) in aqueous medium, hence experimental studies were carried out by the authors to predict the molecular interactions in amide-water mixtures through measurements of viscosity (η), density (ρ) and ultrasonic velocity (U) at 298.15K. The main purpose of this study is to elaborate the molecular interactions in the studied binary mixtures and

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subsequently to determine the effect of the substituent length of amides. Liquid mixtures containing the amide functional group constitute an important tool in the interpretation of complex molecule of biological interest. In view of the importance mentioned, an attempt has been made to elucidate the molecular as well as structural interactions in the mixtures of amides in an aqueous medium at 298.15K. The excess functions are used to notify significant interactions in the studied binary mixtures.

EXPERIMENTAL

Materials and Methods

All the chemicals used in the present research work were analytical reagent (AR) grade having purity minimum assay of 99.9% purchased from Sigma-Aldrich, Germany and were used without further purification. The purity of the above chemicals was checked by density determination at 298.15K; the uncertainty is less than $\pm 1x10^{-4} g\cdot cm^{-3}$. The binary liquid mixtures of different known compositions were prepared in airtight, narrow mouth ground Stoppard bottles. The density, viscosity and ultrasonic velocity were measured as a function of the composition of the binary liquid mixture of distilled water with Formamide, N-Methylformamide and N, N-Dimethylformamide respectively at 298.15K.

Density Measurements

The density was determined using a high precision ANTON PAAR (Model: DMA5000) digital Densitometer. The weight of the sample was measured using an electronic digital balance with an accuracy of ± 0.01mg (Model: Shimadzu AUW-220D).

Viscosity Measurements

An Ubbelohde viscometer (30ml) was used for the viscosity measurements and efflux time was determined using a digital clock having an accuracy of ± 0.1s.

Ultrasonic Velocity Measurements

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. A Julabo F-32 Cryostat German made, 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.

Theory and Calculations

Excess volumes are determined by:

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

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 compressibilities of liquid mixtures and Φ is volume fraction of pure components.

The excess properties y^E are fitted by the method of nonlinear least squares to a Redlich-Kister type polynomial (5):

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

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

$\sigma y^E = [\sum (y^E_{obs} - y^E_{cal}) / (n\text{-}m)]^{1/2}$ (6)

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

$L_f^E = L_{fmix} - x_1 L_{f1} - x_2 L_{f2}$ (7)

Excess values of the above parameters can be determined using:

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

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

Available volume $V_a = (V_m - V_0) = V_m(1 - U/U_m)$ (9)

Where, $V_m = M/\rho$, is the molar volume, U=Velocity, $V_0 = M/\rho_0$ = molar volume at absolute zero temperature and U_m = Schaaf's limiting value taken as 1600m/s for liquids.

RESULTS AND DISCUSSION

In the pure state, water has a high degree of self-association. This association decreases with increasing concentration of amides, when amides are mixed with water then there is an interaction between their individual functional groups (H-O-H and –HN–C=O). The presence of electron withdrawing group in amides decreases electron densities on oxygen atom in water. The polarity of water is less hence their degree of self-association is less as compared to amides. The experimental values of density, viscosity and ultrasonic velocity for the aqueous solutions of studied amides at 298.15K are given in Table-1.The values of excess thermodynamic and acoustical parameters for aqueous solutions of studied amides at 298.15 K are presented in Table-2 and 3.

Table-1: Values of Molality (m), Density (ρ), Viscosity (η), Ultrasonic Velocity (U) for Binary Systems of FA, MFA, DMF (1) + Water (2) at 298.15K.

m /mol·kg^{-1}	ρ (gm·cm^{-3})	ηx10^3 (N·s·m^{-2})	U (m·s^{-1})
Formamide +Water			
0.00000	0.99704	0.8902	1497.70
0.10321	0.9977	0.8928	1497.86
0.20072	0.99834	0.8950	1500.88
0.30832	0.99903	0.8975	1502.58
0.40504	0.99965	0.8996	1504.11
0.58532	1.00079	0.9038	1506.97
0.60910	1.00094	0.9043	1507.34
0.70500	1.00151	0.9065	1508.86
0.80864	1.00215	0.9088	1510.50
0.93966	1.00293	0.9118	1512.57
N-Methylformamide+Water			
0.00000	0.99704	0.8902	1497.70
0.10209	0.99727	0.9007	1500.28
0.20687	0.99752	0.9115	1502.94
0.30257	0.99776	0.9213	1505.36
0.41497	0.99803	0.9329	1508.21
0.50819	0.99825	0.9425	1510.57
0.61377	0.99849	0.9534	1513.24

0.71210	0.99874	0.9636	1515.73
0.80547	0.99896	0.9732	1518.09
0.91062	0.99921	0.9841	1520.76
N,N-Dimethylformamide+Water			
0.00000	0.99704	0.8902	1497.70
0.09987	0.99693	0.9048	1501.95
0.20105	0.99682	0.9218	1506.25
0.30286	0.99673	0.9392	1510.58
0.41502	0.99663	0.9562	1515.35
0.51802	0.99656	0.9727	1519.73
0.60646	0.99650	0.9865	1523.49
0.70667	0.99644	1.0014	1527.75
0.73868	0.99642	1.0066	1529.12
0.91098	0.99634	1.0333	1536.44

Table-2: Values of Molality (m), Excess Volume (V^E), Viscosity Deviations ($\Delta\eta$), Deviations in Isentropic Compressibility (ΔK_S) for Binary Systems of FA, MFA, DMF (1) + Water (2) at 298.15K.

m/ $mol\cdot kg^{-1}$	$V^E x10^6$ ($m^3\cdot mol^{-1}$)	$\Delta\eta x10^3$ ($Kg\cdot m^{-1}\cdot s^{-1}$)	ΔK_S x10^{11} ($m^2\cdot N^{-1}$)
Formamide +Water			
0.00000	0.0000	0.0000	0.00
0.10321	-0.0020	-0.2113	-0.02
0.20072	-0.0043	-0.4192	-1.70
0.30832	-0.0068	-0.633	-2.60
0.40504	-0.0092	-0.8277	-3.40
0.58532	-0.0134	-1.1795	-4.89
0.60910	-0.0140	-1.2277	-5.08
0.70500	-0.0158	-1.4151	-5.86
0.80864	-0.0181	-1.6171	-6.70
0.93966	-0.0207	-1.8803	-7.74
N-Methylformamide+Water			
0.00000	0.0000	0.0000	0.00
0.10209	-0.0041	0.8780	-1.95
0.20687	-0.0085	1.7927	-3.89
0.30257	-0.0125	2.6337	-5.65
0.41497	-0.0174	3.6219	-7.70
0.50819	-0.0214	4.4460	-9.38
0.61377	-0.0257	5.3706	-11.28
0.71210	-0.0303	6.2412	-13.05
0.80547	-0.0343	7.0596	-14.72

0.91062	-0.0388	7.9896	-16.57
N,N-Dimethylformamide+Water			
0.00000	0.0000	0.0000	0.00
0.09987	-0.0054	1.4672	-2.93
0.20105	-0.0113	3.1788	-5.83
0.30286	-0.0171	4.9421	-8.72
0.41502	-0.0235	6.6617	-11.87
0.51802	-0.0295	8.3230	-14.73
0.60646	-0.0349	9.7153	-17.18
0.70667	-0.0408	11.222	-19.92
0.73868	-0.0430	11.7462	-20.81
0.91098	-0.0533	14.4442	-25.45

Table-3: Values of Molality (m), Excess Values of Free Length (L_f^E), Available Volume (Va^E), and Internal Pressure (π_i^E) for Binary Systems of FA, MFA, DMF (1) +Water (2) at 298.15K.

m /mol·kg^{-1}	L_f^E x 10^{-10} m	V_a^E x 10^{-6} m^3·mol^{-1}	π_i^E x 10^6 N·m^{-1}
Formamide +Water			
0.00000	0.0000	0.0000	000.00
0.10321	-0.0001	0.003	-303.34
0.20072	-0.0010	-0.027	-808.32
0.30832	-0.0015	-0.042	-1197.82
0.40504	-0.0020	-0.055	-1548.11
0.58532	-0.0029	-0.080	-2183.78
0.60910	-0.0030	-0.084	-2268.78
0.70500	-0.0034	-0.097	-2609.35
0.80864	-0.0039	-0.112	-2970.32
0.93966	-0.0045	-0.131	-3438.88
N-Methylformamide+Water			
0.00000	0.0000	0.0000	000.00
0.10209	-0.0008	-0.034	297.95
0.20687	-0.0017	-0.070	679.35
0.30257	-0.0024	-0.102	1039.66
0.41497	-0.0033	-0.140	1449.75
0.50819	-0.004	-0.172	1808.41
0.61377	-0.0048	-0.208	2152.67
0.71210	-0.0056	-0.242	2509.42
0.80547	-0.0063	-0.275	2789.97
0.91062	-0.0071	-0.312	3152.13
N,N-Dimethylformamide+Water			

0.00000	0.0000	0.0000	000.00
0.09987	-0.0012	-0.052	399.62
0.20105	-0.0025	-0.106	1098.31
0.30286	-0.0037	-0.160	1911.13
0.41502	-0.0050	-0.220	2440.1
0.51802	-0.0062	-0.276	3042.19
0.60646	-0.0073	-0.325	3451.66
0.70667	-0.0084	-0.380	3881.37
0.73868	-0.0088	-0.398	4030.65
0.91098	-0.0108	-0.495	4869.15

From Table-1 it is seen that, 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.

The observed V^E may be analyzed in terms of several effects, which may be categorized as physical, chemical and geometrical contributions[5].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 the geometrical fitting of one component into other[10].

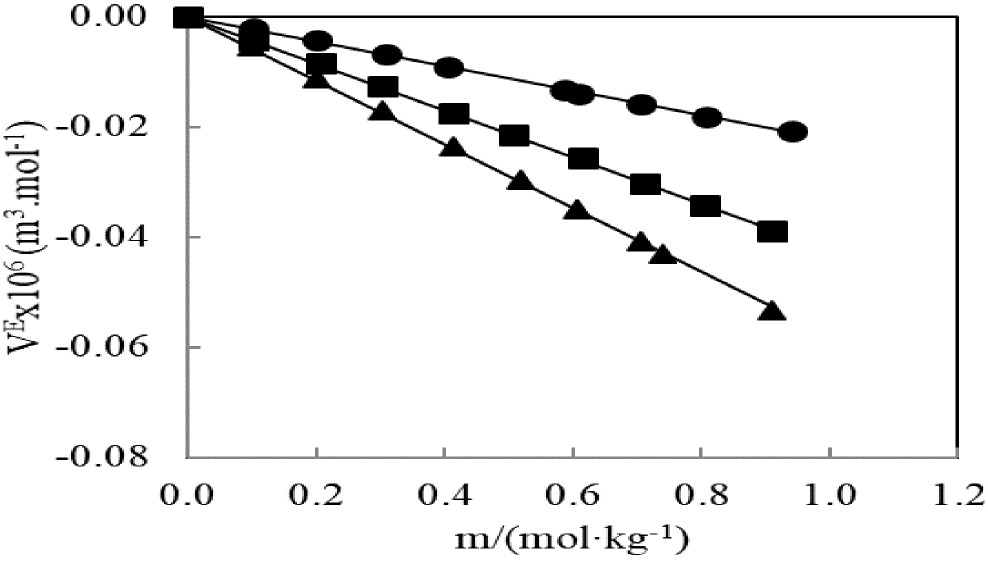

Fig.-1: Variation of Excess Volume (V^E) as a Function of Molality (m) of Amides in Aqueous Solutions at 298.15K. : FA (●); MFA (■); and DMF (▲).

In all studied systems, no positive deviations of V^E have been observed, attributed strong molecular interactions between the unlike molecules. Generally, when two solvents are mixed, the molecular interactions held will depend upon the type and nature of molecules. The positive excess volumes attribute structure breaking interactions while negative excess volumes attribute structure making interactions[11].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 and signifies noticeable effect due to the substitution of H by -CH_3 at the N site. The DMF (*tert.amides*) gives large V^E than MFA (*sec. amides*) and later larger than FA (*pri.amides*).DMF does not show significant H-bonding ability as DMF is not associated in a pure state, but they are sufficiently polar that the pure liquids presumed to be highly structured. However, FA and MFA are H-bonded, hence it could be considered that their V^E values are consistent with substantial variation of amide self-aggregation in switching from pure liquids to water mixtures.Begonia Garcia and others observed V^E values for DMF-Water mixtures more negative than those of alcohol mixtures suggested that the structure of tertiary amides in water mixtures are even more compact than in pure state. Primary amides (FA) and secondary amides (MFA) are self associated to a greater extent than tertiary amides (DMF), which justify the more negative value of DMF[12].

Figure-2 represents a plot of the variation of excess viscosity (Δη) as a function of molality (m) for all three studied aqueous amide systems at 298.15K, positive values are observed for MFA and DMF-Water systems, while negative values are observed for FA-Water system. This trend of positive Δη values in increasing order often found in systems of polar unlike molecules, as in ethanol-water, dioxane-water[13], diethylamine-water[14] and DMSO-water[15] and N, N-bisubstituted amides[16]. The positive values of Δη in the MFA and DMF aqueous mixtures suggests strong hetero-association by multiple H-bonding much in excess of weak association in the pure MFA and DMF. In contrast, Garcia observed the Δη values are negative in amide-alkanol systems, except FA-Propanol-Pentanol and changed from negative to positive with increasing concentration of alcohol[12]. From the above discussion, it is revealed that secondary (MFA) and tertiary (DMF) amides interact strongly with water.

In the present investigation, the values of Δη are more positive at higher concentration of the amides (Fig.-2) provide additional evidence for the existence of strong interactions like dipole-dipole type between components of liquid mixtures. The large positive values of excess viscosity can be attributed to the presence of the dispersion, induction and dipolar forces between the components while observed negative values infer the existence of dispersion, induction and dipolar forces.The magnitude of Δη in MFA and DMF-Water system is positive and shows a linear increase with the concentration of the amides indicates that the specific interactions leading to the formation of complexes in liquid mixtures tend to make Δη values positive.

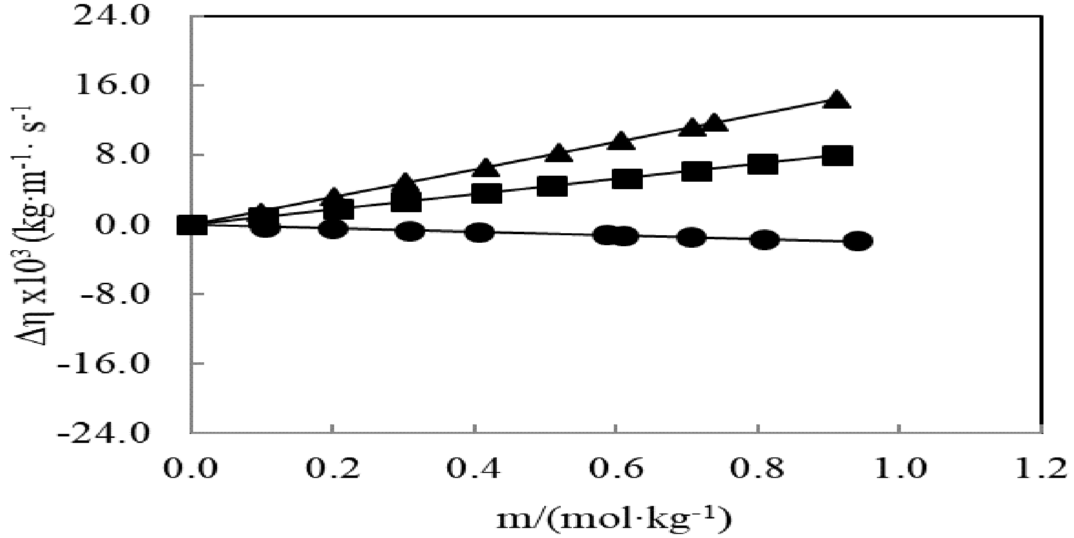

Fig.-2: Variation of Viscosity Deviation (Δη) as a Function of Molality (m) of Amides in Aqueous Solutions at 298.15K: FA (●); MFA (■); and DMF (▲).

It is observed from Figure-3 that values of ΔKs are negative for all studied systems over the whole composition range at 298.15K.This behavior indicates specific interactions between amide and water molecules. The ΔKs values depend upon several contributions of physical and chemical nature[17]. More negative values suggest stronger interactions between unlike molecules like the formation of hydrogen bonds, the formation of charge transfer complexes and stronger dipole-dipole interactions between component molecules[18]. The deviations of bisubstituted amide (DMF) are greater in absolute values than mono-substituted (MFA) and these than un-substituted (FA) [19].

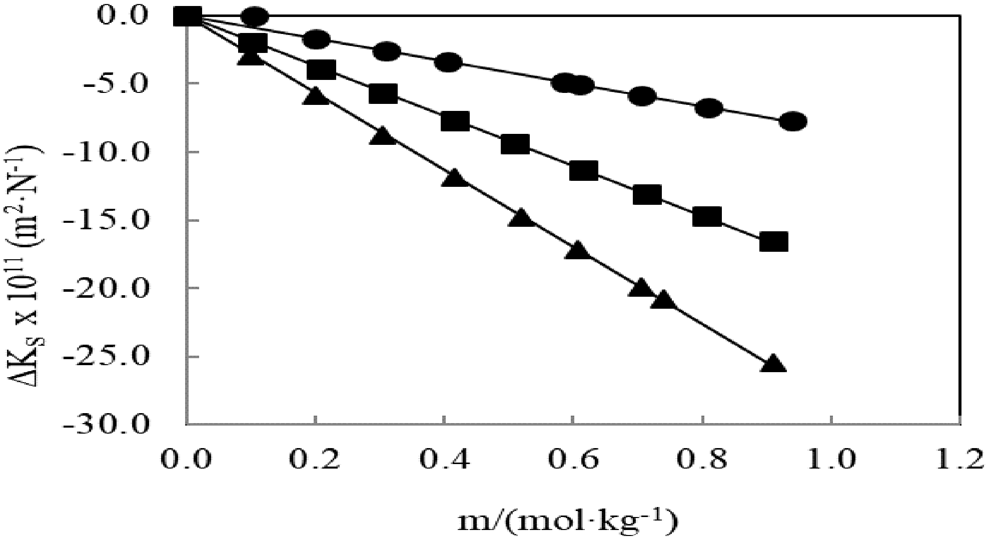

Fig.-3: Variation of Deviation in Isentropic Compressibility (ΔK_S) as a Function Molality (m) of Amides in Aqueous Solutions at 298.15K: FA (●); MFA (■); and DMF (▲).

Table-1shows increase in ultrasonic velocity in solutions and it depends upon variations in molecular free length due to the interaction of components. Excess free length L_f^E have very small values and decrease with increasing concentration of solutes for all studied systems similarly, values of excess available volume(V_a^E) for all studied systems are found negative. The observed negative and positive values for excess parameters such as L_f^E ,V_a^E and π_i^E respectively for amide-water mixtures shown in Table-3 indicates presence of specific interaction between water and amide molecules in these mixtures and is due to existence of dipole-dipole or dipole-induced interactions, proper interstitial accommodation and orientational ordering leading to more compact structure making negative contribution to $L_f^E$and $V_a^E$for all systems and positive contribution except FA to π_i^E(Figure- 4 to 6)[20].

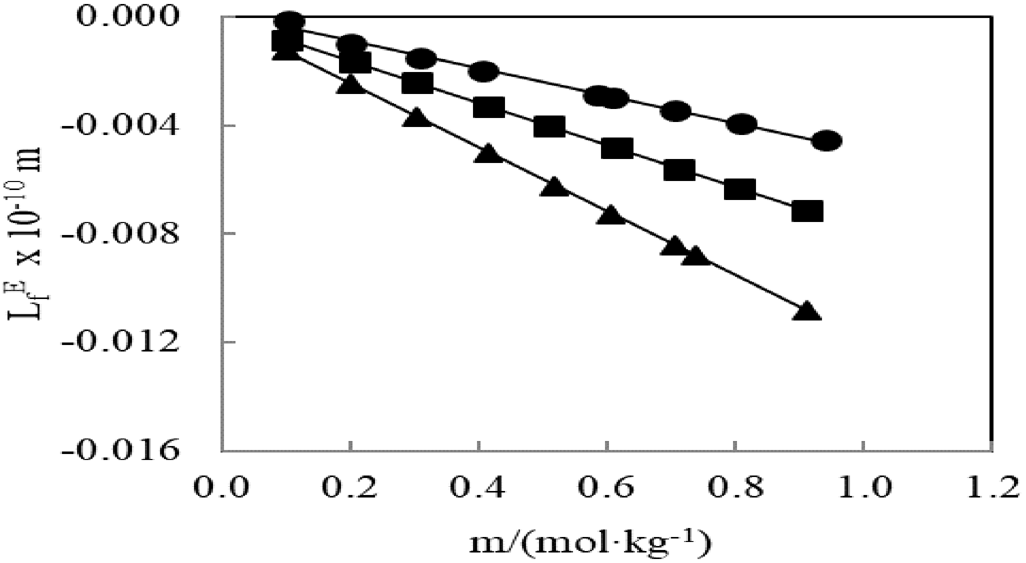

Fig.-4: Variation of Excess Free Length (L_f^E) as a Function of Molality (m) of Amides in Aqueous Solutions at 298.15K. : FA (●); MFA (■); and DMF (▲).

It is noticed from the Figure-6 that excess internal pressure (π_i^E) values increased with increasing concentration of solute in mixtures of MFA and DMF-Water systems at 298.15K, indicating strong solute-solvent interactions in solution. The nature of π_i^E plot is quite same as that of $\Delta\eta$ showing positive

values of $\Delta\eta$ and $\pi_i^E$for MFA and DMF-Water mixtures, while negative values for FA-Water mixtures provides evidence that, secondary (MFA) and tertiary amides (DMF) interact strongly with water.
Finally, the Δk_S,$L_f^E$and V_a^E values are negative over the entire composition range of the amides at 298.15K, these plots are linear with a negative slope. The values of Δk_S, L_f^EandV_a^E follow the same order of interactions as that of V^E. FA shows weakest while DMF shows the strongest interactions. These negative values may be attributed to the existence of dipolar forces between unlike molecules as well as due to hydrogen bonding,dipole-dipole interactions etc. between water and amide molecules or due to the geometrical fitting of one component into another related to the difference in size and shape of the molecules[18].

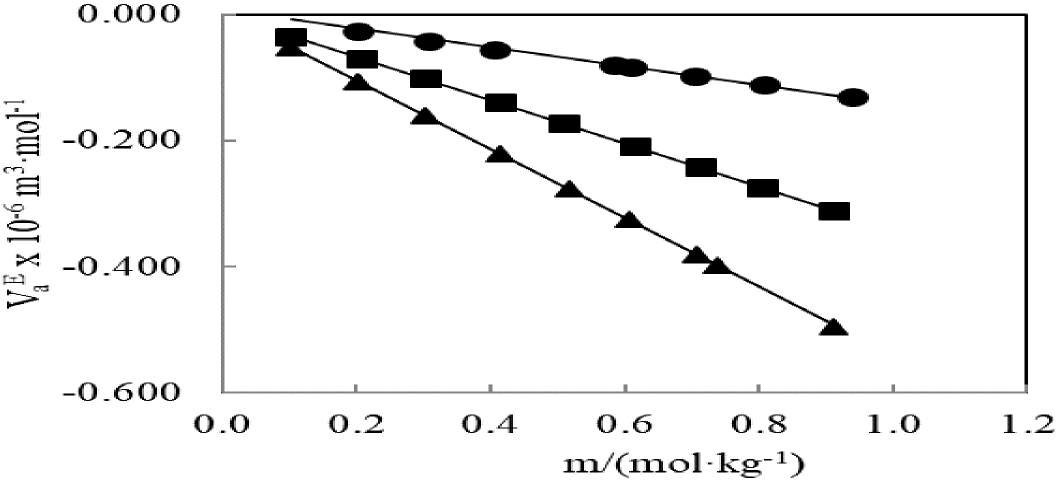

Fig.-5: Variation of Excess Available Volume (V_a^E) as a Function of Molality (m) of Amides in Aqueous Solutions at 298.15K: FA (●); MFA (■); and DMF (▲).

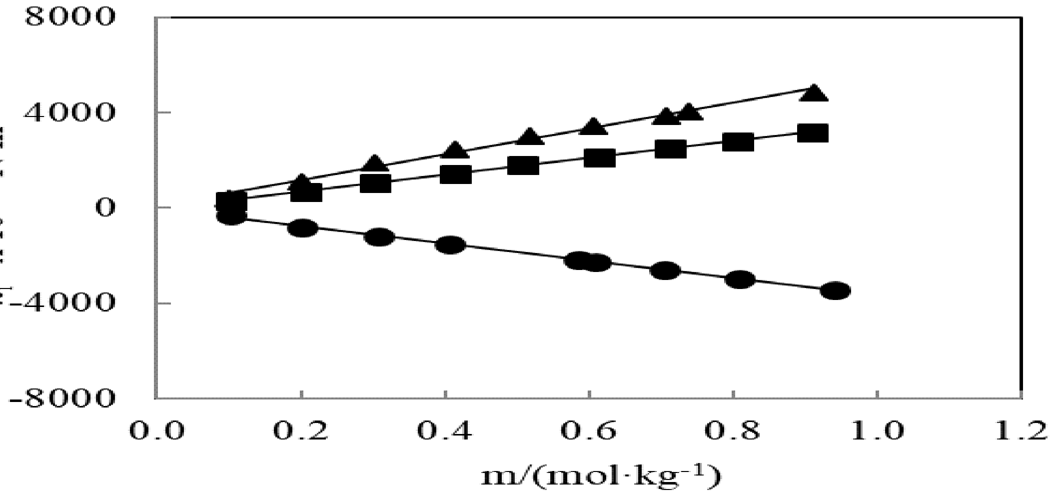

Fig.-6: Variation of Excess Internal Pressure (π_i^E) as a Function of Molality (m) of Amides in Aqueous Solutions at 298.15K: FA (●); MFA (■); and DMF (▲).

CONCLUSION

The experimental data of ultrasonic velocity (U), density (ρ) and viscosity (η) are reported for binary aqueous mixtures of FA, MFA and DMF over the entire range of mole fractions at 298.15K.Calculated viscosity deviation, excess V^E, Δk_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 DMF-Water mixture which may be due to strong hydrogen bond formation and more basicity and weak molecular interaction that exists in the FA-water mixtures, which may be due to the dominance of dispersion forces and dipolar interaction between the unlike molecules.

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