

## Excess Thermodynamic Properties Of Ternary Liquid Mixtures Of some Aliphatic Alcohols At 303.15, 308.15 And 313.15 K.

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### ABSTRACT

Ultrasonic velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) for the ternary liquid mixtures of equimolar ethylene glycol and glycerol (EG+Gly), ethyl alcohol and glycerol (EA+Gly), ethyl alcohol and ethylene glycol (EA+EG) systems with EA, EG and Gly, respectively have been measured as a function of the composition at 303.15, 308.15 and 313.15 K. The experimental data have been used to calculate some excess thermodynamical parameters, such as viscosity ( $\eta^E$ ),

adiabatic compressibility ( $\beta^E$ ), free length ( $L_f^E$ ), free volume ( $V_f^E$ ), internal pressure( $\pi_i^E$ ) and Gibb's free energy( $\Delta G^E$ ). The viscosity data have been correlated by Grunberg and Nissan correlation equation. The results have been used to discuss the nature and strength of heterogeneous H-bond interactions in the presence of mono, di and tri hydric alcohol constituent of the mixture.

### Keywords:

Ultrasonic velocity, Adiabatic compressibility, Free length, Free volume, Gibb's free energy

### INTRODUCTION

Ultrasonic studies have found wide applications owing to their ability to characterize the physico-chemical behavior of solutions. The knowledge of physico-chemical properties of non-aqueous ternary liquid mixtures has relevance in theoretical and applied area of research and such results are frequently used in design process (flow, mass transfer or heat transfer calculations) in many chemical and industrial process (1). Studies of thermodynamic properties of ternary mixture are of considerable interest in the fundamental understanding of the nature of interactions between the unlike molecules. In recent years, the theoretical and experimental investigations of excess and deviation functions are taken as interaction parameters to

improve the results (2). Our research is concerned to the systematic study of molecular interactions in the ternary mixtures, which are important in many fields of industrial and biological processes. Mixed solvents find practical applications as they provide wide range of mixtures with desired properties (3). The formation of molecular clusters and network structures due to strong intermolecular interactions through H-bonds in alcohols results in their complicated molecular structures in liquid state. The liquids were selected on the basis of their industrial use (4). Alkanol molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups (5), where as alkanediol molecules are self-associated through inter and intra hydrogen bonding. Ethyl alcohol is an important ingredient and has widespread use as a base chemical for other

organic compounds. It is also used in medical wipes and alcoholic beverages. Ethylene glycol are important liquids which find a variety of applications in pharmaceuticals, cosmetics etc. Glycerol is used in industry and in many other applications, including antifreeze, detergents, cosmetics and pharmaceutical products. It also serves in research as a biological cryoprotectant (6). In last two decades, the characterization of heterogeneous interactions between associating polar liquids in binary mixtures over the entire concentration range using other studies have been the subject of several investigations (7,8). The H-bond has a considerable effect on the excess thermodynamical parameters of the ternary mixtures of the associating molecules. The evaluation of excess thermodynamical parameter properties over the entire concentration range provides information about the formation of heterogeneous molecular interaction and also about the molar ratio corresponding to the formation of the strongest H-bonded interactions between the mixture constituents. In the present work, density, viscosity and ultrasonic measurements on the binary and ternary mixtures of mono-, di-, and trihydric aliphatic alcohol at different temperatures were carried out, in order to get ideas about the formation of the strongest H-bonded structure with increases in the number of hydroxyl group over the entire concentration variation of the mixture constituents.

To the best of our knowledge no literature data are available for the densities, viscosities and ultrasonic velocities of the binary and ternary mixtures reported here and at different temperatures.

## MATERIALS AND METHODS

All the chemical used are of analytical reagent (AR) and spectroscopic reagent (SR) without further purification. The purities of the above chemicals were checked by density determination at 303.15, 308.15, 313.15  $\pm$  0.1 K, which showed an accuracy of  $\pm 1 \times 10^{-4}$  gcm<sup>-3</sup> with the earlier values (26-36). The ternary 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 ternary liquid mixture at 303.15, 308.15 and 313.15 K for mixed solvent systems in which Ethyl alcohol, Ethylene glycol and Glycerol were added to the equimolar EG+Gly, EA+Gly and EA+EG binary mixtures. The density was determined using a specific gravity bottle by relative measurement

method with an accuracy of  $\pm 0.01$  kgm<sup>-3</sup>. The weight of the sample was measured using electronic digital balance with an accuracy of  $\pm 0.1$ mg (Model: SHIMADZU AX-200). An Ostwald's viscometer (10ml) was used for the time flow measurement. Efflux time was determined using a digital chronometer within  $\pm 0.01$  s. An ultrasonic interferometer having the fixed frequency of 3MHz (Mittal Enterprises, New Delhi, Model: F-81) with an overall accuracy of  $\pm 0.1\%$  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. The accuracy in the temperature measurement is  $\pm 0.1$ K.

## THEORY

Various acoustical and thermodynamical parameters calculated from the measured data are as follows:

Adiabatic compressibility

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

Intermolecular free length

$$L_i = K_j \beta^{1/2} \quad (2)$$

where  $K_j$  is temperature dependent constant. Its value is  $631 \times 10^{-6}$  and  $636 \times 10^{-6}$  and  $642 \times 10^{-6}$ , respectively at 303.15, 308.15 and 313.15 K.

Free volume

$$V = \left( \frac{M_{\text{eff}} U}{k \eta} \right)^{3/2} \quad (3)$$

where  $M_{\text{eff}}$  is the effective molecular weight ( $M_{\text{eff}} = \sum_i M_i X_i$  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  $4.28 \times 10^9$  for all liquids.

Internal Pressure

$$\pi_i = bRT \left( \frac{k \eta}{U} \right)^{1/2} \left( \frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}} \right) \quad (4)$$

where  $b$  is the cubic packing which is assumed to be 2 for all liquids,  $R$  is the universal gas constant and  $T$  is absolute temperature.

Gibb's free energy

$$\Delta G = K_B T \ln \left( \frac{K_B T \tau}{h} \right) \quad (5)$$

where  $K_B$  is Boltzmann's constant ( $1.38 \times 10^{-23} \text{ JK}^{-1}$ ),  $h$  the Planck's constant ( $6.626 \times 10^{-34} \text{ Js}$ ) and  $\tau$  is the relaxation time ( $\tau = \left(\frac{4}{3}\right) \eta \beta$ ).

Excess values of the above parameter can be determined using

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (6)$$

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

Grunberg and Nissan (9) formulated the following relation between the viscosity of a binary liquid mixture and pure components.

$$\ln \eta_{\text{mix}} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 d \quad (7)$$

on applying to a ternary liquid mixture, this equation takes up the form

$$\ln \eta_{\text{mix}} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_3 \ln \eta_3 + X_1 X_2 X_3 d \quad (8)$$

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

## RESULTS AND DISCUSSION

The values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of pure liquids and liquid mixtures at 303.15, 308.15 and 313.15 K are given in Tables 1 - 2. The values of excess viscosity ( $\eta^E$ ), excess adiabatic compressibility ( $\beta^E$ ), excess free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), excess internal pressure ( $\pi_i^E$ ), excess Gibb's free energy ( $\Delta G^E$ ) and Grunberg's interaction parameter ( $d$ ) have been calculated and presented in Tables 3 - 4. Further, the variation of  $V_f^E$  with mole fractions of  $X_3$  at

303.15, 308.15 and 313.15 K are shown in Fig. 1 and the curves are drawn using least square fitting.

The excess thermodynamic properties of mixtures which correspond to the difference between the actual property and the property if the system behaves ideally and, thus are useful in the study of molecular interactions and arrangements in the mixtures. In particular, they reflect the interactions that take place between solute - co-solute and solute-solvent species. The effects which are expected to operate between the component molecules under study are, (i) structural effect which is due to the differences in shape and size of the component molecules (ii) re-orientational effect between component molecules and (iii) energetic effect, i.e., molecular interaction that can be weakened or destroyed or established during the mixing process (10). The excess viscosity (Table 3) is negative through the whole range of concentration in all the three systems. From the analysis and close observation it is found that they increase with increase in mole fraction of  $X_3$  and also with the rising of temperature in systems I and II, but it decreases with increasing the concentration of  $X_3$  in system III. This observed behaviour shows that the existence of molecular interaction between the components of mixture for all the systems studied.

The  $\beta^E$  (Table 3) values are negative, and these values are increasing with increase in mole fraction of  $X_3$ , but it decreases with rising of temperature in all systems studied. However the values of  $\beta^E$  are decreases with increasing the concentration of EA in system I. The observed  $\beta^E$  values depend upon several contributions, which are of physical and or chemical nature (11-12). The physical contributions comprise of dispersion forces and non specific physical (weak)

**Table 1. Comparison of experimental and literature values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) of pure liquids at 303.15, 308.15 and 313.15 K**

Organic liquids	T/K	$\rho / (\text{kg m}^{-3})$		$\eta / (\times 10^{-3} \text{ Nsm}^{-2})$		U / (m.s <sup>-1</sup> )	
		Experimental	Literature	Experimental	Literature	Experimental	Literature
Ethyl alcohol	303.15	785.4	0.7834 <sup>1</sup>	1.0272	0.9944 <sup>2</sup>	1140.4	1132.2 <sup>2</sup>
	308.15	780.6	0.7790 <sup>1</sup>	0.9927	0.9097 <sup>2</sup>	1125.2	1117.0 <sup>2</sup>
	313.15	776.1	0.7746 <sup>1</sup>	0.8985	0.8306 <sup>2</sup>	1110.1	1102.8 <sup>2</sup> 1654.3 <sup>7</sup> (298.15K)
Ethylene glycol	303.15	1114.1	1.1064 <sup>3</sup>	12.9760	13.1544 <sup>4</sup>	1648.8	
	308.15	1108.8	1.1028 <sup>3</sup>	10.2820	10.50 <sup>5</sup>	1633.2	
	313.15	1104.1	1.0984 <sup>3</sup>	9.0230	9.74 <sup>5</sup> 9.1316 <sup>6</sup>	1628.4	
Glycerol	303.15	1257.7	1.25495 <sup>8</sup>	618.9236	622 <sup>9</sup>	1819.3	
	308.15	1254.3		262.4170	266.610 <sup>10</sup>	1774.8	
	313.15	1251.1		194.1140		1766.4	

1 – Bhuiyan et.al., (2007)

2 – Anil Kumar Nain et.al., (2008 )

3 – Saeid Azizion et.al., (2005)

4 – Timmermans et.al., (1935)

5 – Vijayakumar Naidu et.al., (2003)

5 – Tongfan Sun et.al., (2003)

6 – Jerome et.al., (1968)

7 – Cezary M. Kinart et.al., (2009)

8 – Diana M. Cristancho et.al., (2011)

9 – John A. Dean

10 – Davis et.al., (1912)

**Table 2. Values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) at 303.15, 308.15 and 313.15 K for**

Molefraction (X <sub>3</sub> )	$\rho / (\text{kg m}^{-3})$			$\eta / (\times 10^{-3} \text{ Nsm}^{-2})$			U / (m.s <sup>-1</sup> )		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
<b>System – I : Ethylene glycol (X<sub>1</sub>) + Glycerol (X<sub>2</sub>) + Ethyl alcohol (X<sub>3</sub>) [(X<sub>1</sub>)/(X<sub>2</sub>)=1:1]</b>									
0.0000	1202.4	1200.2	1198.9	42.4115	35.0401	29.7558	1763.4	1753.2	1752.5
0.0199	1199.3	1196.9	1193.2	38.8937	31.6523	27.1709	1760.4	1749.5	1747.2
0.0409	1197.2	1193.2	1190.3	37.7220	30.9086	26.2824	1739.7	1735.8	1730.6
0.0597	1185.7	1184.9	1179.3	34.6444	29.4285	25.9319	1736.4	1733.4	1729.2
0.0800	1184.7	1183.7	1177.4	33.1950	28.2449	25.0303	1728.6	1725.6	1720.7
0.1000	1179.5	1176.0	1171.0	31.8064	27.9534	24.0972	1718.1	1714.4	1710.1
<b>System – II : Ethyl alcohol (X<sub>1</sub>) + Glycerol (X<sub>2</sub>) + Ethylene glycol (X<sub>3</sub>) [(X<sub>1</sub>)/(X<sub>2</sub>)=1:1]</b>									
0.0000	1045.4	1043.2	1040.5	11.7719	10.4705	8.8721	1489.8	1484.4	1471.8
0.0199	1049.6	1047.3	1044.0	12.2259	10.5177	9.0789	1497.6	1491.3	1485.9
0.0402	1053.9	1051.1	1046.4	12.4997	10.6528	9.2903	1501.2	1492.7	1487.0
0.0601	1055.9	1053.9	1048.6	12.6330	10.7766	9.3856	1506.5	1498.8	1496.7
0.0804	1059.2	1057.7	1053.9	13.1099	10.9223	9.4791	1512.1	1509.6	1506.4
0.0998	1063.2	1060.8	1056.5	13.6608	11.0121	9.5187	1517.4	1513.0	1511.8
<b>System – III : Ethyl alcohol (X<sub>1</sub>) + Ethylene glycol (X<sub>2</sub>) + Glycerol (X<sub>3</sub>) [(X<sub>1</sub>)/(X<sub>2</sub>)=1:1]</b>									
0.0000	965.5	960.9	956.8	3.6372	3.2751	2.9022	1495.1	1492.6	1489.2
0.0201	978.4	976.3	974.5	4.1976	3.7816	3.3272	1491.6	1488.0	1480.2
0.0399	981.1	980.1	979.5	4.2199	3.8096	3.3489	1487.5	1480.7	1472.2
0.0601	993.7	990.8	987.4	4.8018	4.2506	3.7628	1481.7	1473.2	1466.5
0.0801	999.2	996.1	994.9	5.1824	4.6242	4.0118	1475.2	1468.2	1459.8
0.1006	1004.8	1002.1	999.7	5.6007	4.9470	4.3280	1464.0	1460.1	1450.4

**Table 3. Excess values of viscosity ( $\eta^E$ ), adiabatic compressibility ( $\beta^E$ ), free length ( $L_f^E$ ) and free volume ( $V_f^E$ ) at 303.15, 308.15 and 313.15 K for**

Molefraction ( $X_3$ )	$-\eta^E / (\times 10^{-3} \text{Nsm}^{-2})$			$-\beta^E / (\times 10^{-12} \text{m}^2 \text{N}^{-1})$			$-L_f^E / (\times 10^{-10} \text{m})$			$-V_f^E / (\times 10^{-9} \text{m}^3 \text{mol}^{-1})$		
	303.15K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
<b>System – I : Ethylene glycol (<math>X_1</math>) + Glycerol (<math>X_2</math>) + Ethyl alcohol (<math>X_3</math>) [(<math>X_1</math>)/(<math>X_2</math>)=1:1]</b>												
0.0000	273.53	101.31	71.81	11.75	24.54	27.29	3.04	4.36	4.90	0.61	0.92	1.06
0.0199	270.87	101.99	72.38	30.01	36.96	39.26	4.55	5.85	6.26	1.33	1.61	1.85
0.0409	265.63	100.03	71.36	36.97	46.10	48.22	5.05	6.72	7.05	2.12	2.41	2.75
0.0597	262.41	98.80	69.60	47.11	57.70	60.08	6.17	8.07	8.40	2.83	3.17	3.67
0.0800	257.56	97.28	68.48	58.21	69.20	71.74	7.47	9.39	9.71	3.59	3.94	4.55
0.1000	252.65	94.86	67.40	67.37	77.92	81.53	8.41	10.21	10.68	4.36	4.76	5.43
<b>System – II : Ethyl alcohol (<math>X_1</math>) + Glycerol (<math>X_2</math>) + Ethylene glycol (<math>X_3</math>) [(<math>X_1</math>)/(<math>X_2</math>)=1:1]</b>												
0.0000	298.20	121.26	88.63	178.65	197.43	207.21	16.62	19.09	19.95	17.74	17.87	19.91
0.0199	291.81	118.78	86.66	179.24	197.24	210.86	16.91	19.26	20.72	17.53	17.68	19.61
0.0402	285.60	116.22	84.68	177.74	193.72	206.30	16.82	18.93	20.24	17.25	17.52	19.36
0.0601	279.59	113.67	82.81	175.57	192.42	206.60	16.74	18.94	20.34	16.98	17.28	18.99
0.0804	273.11	111.09	80.95	174.35	194.05	207.99	16.76	19.41	20.97	16.70	16.82	18.63
0.0998	266.61	108.57	79.14	173.19	191.24	205.81	16.79	19.20	20.87	16.48	16.60	18.24
<b>System – III : Ethyl alcohol (<math>X_1</math>) + Ethylene glycol (<math>X_2</math>) + Glycerol (<math>X_3</math>) [(<math>X_1</math>)/(<math>X_2</math>)=1:1]</b>												
0.0000	3.36	2.36	2.06	191.25	207.85	222.30	20.22	22.17	23.76	10.07	9.24	9.86
0.0201	15.42	6.99	5.42	186.92	203.93	216.46	19.65	21.67	22.97	11.76	11.46	12.23
0.0399	27.25	12.10	9.18	177.37	192.73	205.03	18.29	20.09	21.37	11.23	10.79	11.67
0.0601	38.92	16.79	12.55	171.36	184.63	196.41	17.46	18.97	20.18	12.40	11.92	13.17
0.0801	50.77	21.56	16.08	161.57	175.51	186.91	16.07	17.10	18.87	12.75	12.49	13.57
0.1006	62.59	26.37	19.55	148.82	164.71	174.33	14.26	16.18	17.10	13.07	13.03	14.09

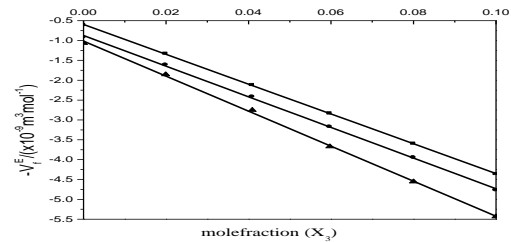
**Table 4. Excess values of internal pressure ( $\pi_i^E$ ) Gibb's free energy ( $\Delta G^E$ ) and Grunberg's interaction parameter (d) at 303.15, 308.15 and 313.15 K for**

Molefraction ( $X_3$ )	$-\pi_i^E / (\times 10^8 \text{Nm}^{-2})$			$\Delta G^E / (\times 10^{-21} \text{KJ mol}^{-1})$			d		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
<b>System – I : Ethylene glycol (<math>X_1</math>) + Glycerol (<math>X_2</math>) + Ethyl alcohol (<math>X_3</math>) [(<math>X_1</math>)/(<math>X_2</math>)=1:1]</b>									
0.0000	33.62	16.18	12.96	3.36	2.01	1.85	3.99	2.57	2.36
0.0199	33.66	16.77	13.43	3.43	2.18	1.98	155.21	88.67	79.96
0.0409	32.49	15.98	12.85	3.19	1.97	1.81	74.50	49.15	43.81
0.0597	32.61	15.78	12.23	3.22	1.91	1.59	51.48	34.95	28.72
0.0800	31.74	15.27	11.73	3.09	1.81	1.47	37.55	27.29	22.21
0.1000	30.91	14.36	11.32	2.94	1.54	1.34	29.09	21.06	18.29
<b>System – II : Ethyl alcohol (<math>X_1</math>) + Glycerol (<math>X_2</math>) + Ethylene glycol (<math>X_3</math>) [(<math>X_1</math>)/(<math>X_2</math>)=1:1]</b>									
0.0000	40.51	22.45	18.78	3.80	2.47	2.39	3.47	1.73	1.59
0.0199	39.32	21.94	18.24	3.61	2.46	2.32	147.97	87.32	76.45
0.0402	38.25	21.32	17.61	3.47	2.35	2.17	73.26	43.14	36.51
0.0601	37.36	20.75	17.18	3.37	2.28	2.12	49.14	28.44	24.04
0.0804	36.14	20.18	16.70	3.17	2.22	2.09	35.50	20.94	17.79
0.0998	34.86	19.62	16.29	2.95	2.15	2.04	26.99	16.66	14.29
<b>System – III : Ethyl alcohol (<math>X_1</math>) + Ethylene glycol (<math>X_2</math>) + Glycerol (<math>X_3</math>) [(<math>X_1</math>)/(<math>X_2</math>)=1:1]</b>									
0.0000	2.45	1.83	1.77	0.20	0.86	0.95	0.02	0.10	0.08
0.0201	3.36	2.02	1.83	0.78	0.59	0.68	7.68	16.75	14.85
0.0399	5.47	3.33	2.96	1.10	0.84	0.92	6.56	3.75	0.79
0.0601	6.43	3.77	3.23	0.94	0.68	0.71	2.56	1.59	1.92
0.0801	7.88	4.45	3.89	0.96	0.62	0.72	3.56	1.01	0.30
0.1006	9.28	5.23	4.45	0.95	0.61	0.64	4.22	0.18	0.17

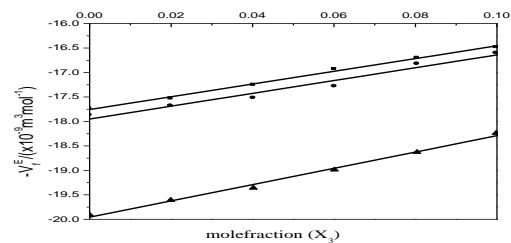
interactions that lead to positive  $\beta^E$  values; physical contribution is also due to geometrical effect allowing the fitting of molecules of different size into each other's structure resulting in negative  $\beta^E$  values. Chemical contributions involve breaking up of the hydrogen-bonded structure (s), resulting in positive  $\beta^E$  values and specific interactions such as the formation of hydrogen bonds, formation of charge transfer complex and strong dipole-dipole interactions between component molecules resulting in negative  $\beta^E$  values. Mixing of EA with binary mixture of (EG+Gly) would induce mutual dissociation of the hydrogen-bonded structures present in pure liquids with subsequent formation of (new) H-bonds between EA and (EG+Gly) molecules in the mixture (13-14), resulting to decrease in the compressibility of the mixture, and hence negative  $\beta^E$  values.

From the variation of excess free length (Table 3) it was observed that the  $L_f^E$  values are negative over the entire mole fraction range and even with rising of temperature. The  $L_f^E$  value are increases with increasing of the concentration of EG and Gly but it decreases with increasing the concentration of EA as well as temperature in all system studied. According to Kannappan *et al.*, (15) negative value of  $L_f^E$  indicates that sound waves cover longer distances due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort *et al.*, (14) indicated that the positive excess values of free length should be attributed to the dispersive forces and negative excess values should be due to charge transfer and hydrogen bond formation. In the present study, it is found that the negative contribution of  $L_f^E$  in all the three systems prevails with the existence of strong H-bond interaction. The magnitude of  $L_f^E$  values follows the sequence: EA>EG>Gly. Fig. 4 shows qualitative picture of the excess free volume for the three ternary liquid systems.

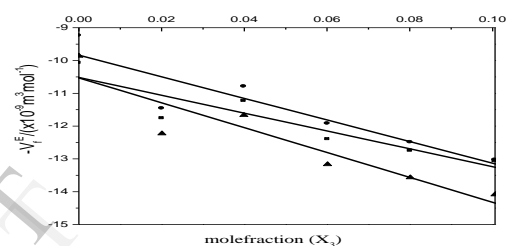
The  $V_f^E$  (Fig.1) values for all the three systems are found to be negative. These values are decreases with increasing the mole fractions of EA and Gly as well as temperature in all systems studied, but it found to increase with the addition of EG. These results can be explained in terms of molecular interaction, structural effect and interstitial accommodation along with changes in free volume. The sign  $V_f^E$  depends upon the relative strength between the contractive forces and expansive forces.



Sys-I: Ethylene glycol ( $X_1$ ) + Glycerol ( $X_2$ ) + Ethyl alcohol ( $X_3$ )



Sys-II: Ethyl alcohol ( $X_1$ ) + Glycerol ( $X_2$ ) + Ethylene glycol ( $X_3$ )



Sys-III: Ethyl alcohol ( $X_1$ ) + Ethylene glycol ( $X_2$ ) + Glycerol ( $X_3$ )

**Fig.1. Variation of excess freevolume ( $v_f^E$ ) of (EG+Gly) , (EA+Gly) and (EA+EG) equimolar solvent system with mole fraction of mono, di and trihydric alcohols at (■)303.15, (●)308.15 and (▲) 313.15 K .**

The factors that cause expansion in volume are following:

- (i) dispersion force.
- (ii) steric hindrance of component molecules.
- (iii) unfavorable geometric fitting.
- (iv) electrostatic repulsion, etc.,

The negative part of  $V_f^E$  curves of the system asserts that the combined effect of the factors responsible for volume contraction out weigh the combined effect of the factors causing volume expansion and vice-versa (16). Adgaonkar *et al.*, (17) showed positive value of  $V_f^E$ , indicating the existence of weak molecular interaction in the liquid mixtures. Fort *et al.*, (14) noticed that negative excess free volume tends to decrease as the strength of the interaction between unlike molecules increases although they are not parallel with the excess compressibilities. However, in the present study the observed behavior of  $V_f^E$  shows that the strength of molecular interaction increases with increasing of mono, di and trihydric alcohols, but it is lesser with increasing of temperature.



In the study of liquid mixtures the variation of internal pressure may give some reliable information regarding the nature and strength of the forces existing between the molecules. When two interacting molecules are having some sort of attractive forces like that of hydrogen bonding, the result in the increase of internal pressure. In fact, the internal pressure is a broader concept and is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to overall cohesion of the liquid system. In all the three systems the variation of excess internal pressure (Table 4) are negative and it found to increase with increasing the mole fraction of EA and EG as well as temperature too but it decreases with increasing of Gly concentration. The negative values of  $\pi_i^E$ , indicate that only dipolar forces are operating between the unlike molecules. Further the observed behavior of  $\pi_i^E$  values reveals that the strengthening of cohesive forces results perhaps due to making up the structure of the solvent.

The values of excess Gibb's free energy (Table 4) are found to be positive and these values are decreases with increasing the mole fraction of  $X_3$  and also with rising of temperature in all systems studied. According to Reed *et al.*, (18) the positive  $\Delta G^E$  may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative values may be ascribed to the dominance to dispersion forces (19). In the present study the observed behavior of  $\Delta G^E$  shows that the formation of H-bond heterogeneous interactions between the components of unlike molecules. EA, EG and Gly molecules exist in self-associated structures through H-bonds with parallel (same direction) dipole alignment in their pure liquid state (20). Self-association depends not only on the steric arrangement of the respective groups, but is also sensitive to the size and shape of the polar molecules. The ethyl alcohol molecule has one -OH group but forms higher order self-associated structures, which results the linear polymeric structures with a switch-over type of molecular reorientation throughout their homogeneous structures (21-22). The molecules of ethylene glycol have at both ends hydroxyl groups with a gauche conformation, which results in intra molecular H-bonding, and hence probably only one -OH group of the EG molecule can interact with neighboring molecules through a H-bond (23). The glycerol molecule contains two primary alcohol groups and one secondary alcohol group, but the H-bond formation through the secondary alcohol group results in the cross linkage H-bonded structures (three-dimensional structures) in the pure liquid state of glycerol (24).

The interaction parameter 'd' in Grunberg *et al.*, (9) equation is a measure of the strength of interaction between the mixing components. d-values were said

to indicate various types of interaction (25) 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 Table 4 that d-values are positive in all the three systems studied. It is seen that the values of 'd' increase with the increasing of mole fraction of  $X_3$  for every mixtures and the same decrease with rising of temperature. Further the increasing behavior of d-values exhibits the increasing the strength of molecular interaction between the unlike molecules. But, however, the strength of interaction gets weakened with the rising of temperature which may be due to decreasing behavior of d-values for all systems studied. The magnitude of 'd' is in order: EA>EG>Gly.

## CONCLUSION

A systematic study of ternary mixture of equimolar EG+Gly, EA+Gly and EA+EG systems with EA, EG and Gly, respectively have been carried out at different concentrations and at different temperatures using ultrasonic measurements. The ultrasonic velocity data and other acoustical parameters give valuable information to understand the solute-solvent interactions in the mixtures. The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components. The variations in excess acoustical parameters with composition indicate the specific H-bond heterogeneous interactions in these mixtures, which decrease with rise in temperature. The strength of interactions tends to be weaker with rising of temperature due to the presence of weak intermolecular forces and thermal dispersion forces. Further, it is observed that the order of interactions in these mixtures depends upon the number of hydroxyl groups. The self association through H-bonds in EA, EG and Gly very anomalously with increase in the number of hydroxyl groups in the alcohol molecules. From the magnitude of ' $L_f^E$ ' and 'd' it can be concluded that the strength of interactions is in the order: EA>EG>Gly.

## REFERENCES:

1. Maravkova.L.; Linck.J., (2003). Excess molar volumes of (benzene+isopropylbenzene, or 1,3,5-trimethylbenzene, or 1,2,4-trimethylbenzene) at temperatures between 298.15 K and 328.15 K. J. Chem. Thermodyn., 35,1139-1149.
2. Aznarez.S.B.; Postigo. M.A., (1998). Excess molar volumes of binary mixtures of acetonitrile with n-alkanols at 25°C. J. Solution Chem., 27,1045-1053(9).
3. Peralta.R.D.; Infante.R.; Cortez.G.; Wisniak.J.,(2004). Density, excess volumes, and

- partial volumes of the binary systems of dimethyl sulfoxide+ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K. *J.Solution Chem.*, 33,339-351.
4. Jasinski.R., (1967). *High Energy Battery*, Plenum, New York.
  5. Krestov.G.A. (1991). *Thermodynamics of solvation* Ellis-Horwood Ltd., England.
  6. Douzou. P., (1977). *Cryobiochemistry*, An introduction, Academic Press, London.
  7. Becker.U.; Stockhausen.M., (1999). A dielectric relaxation study of some mixtures of mono and dihydric alcohols, *J.Mol.Liq.*,81,89-100.
  8. Sengwa.R.J.; Madhvi.; Abhilasha, (2006). comparative study of non-polar solvents effect on dielectric relaxation and dipole moment of binary mixtures of mono alkyl ethers of ethylene glycol and of diethylene glycol with ethyl alcohol, *J.Mol. Liq.*, 123, 92-104.
  9. Grunberg. L.; Nissan. A.H., (1949). Mixture law for viscosity, *Nature*, 164, 799-800.
  10. Giner.B.; Martin. S.; Artigas. H.; Lopez .M.C.; Lafuenta.C., (2006). Study of weak molecular interactions through thermodynamic mixing properties. *J. Phys. Chem.B.*,110,17683-17690.
  11. Ohtaki.H.; Itoh.S.; Yamaguchi.T.; Bratos.S., (1983). Structure of liquid N,N-Dimethyl formamide studied by means of X-Ray diffraction. *Bull. Chem.Soc.Jpn.*,56, 3406-3409.
  12. Iloukhani.H.; Ghorbani.R., (1998). Volumetric properties of N,N-Dimethylformamide with 1,2-Alkanediols at 20°C. *J.Solution Chem.*, 27, 141-149.
  13. Pikkarainan.L., (1983). Densities and viscosities of binary solvent mixtures of N-methylacetamide with aliphatic alcohols. *J.Chem., Eng. Data* , 28, 381-383.
  14. Fort.R.J.; Moore.R., (1965). Adiabatic compressibilities of binary liquid mixtures, *Trans. Faraday Soc.*, 61,2102-2111.
  15. Kannappan.AN.; Palani .R.,(1996). Studies on molecular interaction in ternary liquid mixtures by ultrasonic velocity measurement. *Ind .J .Phys.* , 70B,59-65.
  16. Saleh.M.A.; Akhtar .S.; Ahmed.M.S.; Uddin.M.H., (2002). Excess molar volumes and thermal expansivities in aqueous solutions of dimethyl sulphoxide, THF and 1,4-dioxane. *Phys. & Chem.Liq.*, 40, 620-625.
  17. Adgaonkar.C.S.; Agnihotri, (1989). Theoretical evaluation of ultrasonic velocity in binary liquid mixtures. *Ultrason.*, 27, 248-259.
  18. Reed. T.M.; Taylor.TE.,(1959). Viscosities of liquid mixtures. *J.Phys.Chem.* , 58,63-69.
  19. Qin.Aw.; Haffmann.DE.; Munk.P., (1992). Excess volumes of mixtures of alkenes with carbonyl compounds. *J.Chem. Eng. Data.*, 37, 55-61.
  20. Botcher.C.J.F., (1973), *Theory of Electric Polarization*, Elsevier, Amsterdam, Vol.1.
  21. Sengwa.R.J.; Abhilasha More.N.M., (2003). Dielectric relaxation and molecular dynamics in poly (vinyl pyrrolidone)-ethyl alcohol mixtures in pure liquid state and in non-polar solvent. *Polymer*, 44, 2577-2583.
  22. Sengwa.R.J.; Abhilasha More .N.M. ; Mehrotra.S.C., (2005). Dynamics structure of poly (vinyl pyrrolidone) / ethyl alcohol mixtures studied by time domain reflectometry. *J. Polym. Sci. : Part B : Polym . Phys.* , 43,1134-1143.
  - 23.Sengwa .R.J.; Sankhla.S., (2007). Characterization of heterogeneous interaction in binary mixtures of ethylene glycol oligomer with water, ethyl alcohol and dioxane by dielectric analysis. *J.Mol.Liq.*,130,119-131.
  - 24.Sengwa .R.J.; Abhilasha ; Mehrotra .S.C.; Sharma.B.R., (2004). A comparative dielectric study of poly (vinyl pyrrolidone) in unlike hydroxyl group. *Indian J . Phys.*, 78, 1341-1348.
  - 25.Syamala ; Sivakumar .V.K.; Venkateswaralu.P., (2006) . Volumetric, ultrasonic and viscometric studies of binary mixtures of dimethyl sulphoxide with chloro and nitro substituted aromatic hydrocarbons at T=303. *J.Chem.Thermodyn.*, 38,1553-1562.
  - 26.Bhuiyan. M.M.H.; Ferdaush .J.; Uddin.M.H, (2007). Densities and viscosities of binary mixtures of {dimethyl sulfoxide + aliphatic lower alkanols (C1-C3)} at temperatures from T=303.15 K to T=323.15 K. *J.Chem.Thermodyn.* , 39,675-683.
  27. Anil Kumar Nain ,(2008). Ultrasonic and viscometric studies of molecular interactions in binary mixtures of formamide with ethanol, 1-Propanol, 1,2-ethanediol and 1,2-propanediol at different temperatures. *J. Mol. Liq.*,140,108-116.
  28. Saeid Azizian.; Nowrouz Bashavard, (2005). Surface properties of diluted solutions of cyclohexanol cyclopentanol in ethylene glycol. *J.Colloid and Interface Science* , 282, 428-433.
  29. Timmermans . J.; Hennaut.Roland .M., (1935). Physical constants of 20 organic compounds VII . *J . Chem .Phys.*, 32.501- 505.
  30. Vijayakumar Naidu.B.; Chowdoji Rao .K.; Subha .M.C.S. , (2003) . Densities, viscosities and excess properties for binary mixtures of some glycols and polyglycols in N-Methylacetamide at 308.15 K. *J.Chem. Eng. Data* , 48,625-627.
  31. TongFan Sun.; Amyn S .Teja , (2009). Density, viscosity and Thermal conductivity of aqueous ethylene, diethylene and triethylene glycol mixtures between 290 K and 450 K . *J. Chem. Eng. Data* , 48, 198-202.
  32. Jerome.F.S.; Tseng.J.T.; Fan.L .T.,(1968). Viscosities of aqueous glycol solutions. *J. Chem . Eng . Data* , 13, 496-496.
  33. Cezary M. Kinart ; Piotr Miecznik; Magdelene Klimczak, (2009). Speeds of sound and isentropic compressibilities of (2-ethoxyethanol + ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol) binary mixtures at 298.15 K. *J .Mol .Liq.*, 149,81-85.
  34. Diana M . Cristancho ; Daniel R.Delgado; Fleming Martinez ; Mohammad. A.; Abolghassemi Fakhree.; Abolghasem Jouyban , (2011). Volumetric properties of glycerol + water mixtures at several temperatures and



- correlation with the Jouyban - Acree model , Rev. Colomb .Cienc-Quim. Farm ., 40(1) , 92-115.
35. John A , Dean , (1999), Lange's Hand book of Chemistry., 15<sup>th</sup> Edition.
  36. Davis .P.B.; Jones. H.C., (1912). The absorption spectra of solutions as studied by means of the Radiomicrometer . Z. Phys . Chem .A . , 81,68-70.

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