

# Some Excess Properties of Ternary Liquid Mixture of Water, Methanol, Ethanol at Several Temperatures

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**Abstract:** Densities and viscosities of ternary liquid mixtures of water, methanol, ethanol of volume by volume ratio of 1:1:1 have been measured at 308.15, 313.15., 318.15, 323.15, 328.15, K .From the density and viscosity data the values of various properties, Excess volume ( $V^E$ ) Excess viscosity ( $\mu^E$ ) and Excess Gibb's free energy of activation of flow ( $\Delta G^E$ ) have been determined. On the basis of the values of interaction parameters and various excess properties, the nature of molecular interactions between the components of mixtures has been explained.

**Keywords:** Viscosity, Liquids, Density, Ternary Mixture, Water, Methanol and Ethanol, Excess Volume, Excess Viscosity, Gibb's Free Energy.

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## I. INTRODUCTION

Mixtures of water with aliphatic alcohols are of considerable interest from the viewpoint of the existence of some interaction, such as hydrogen bonding between water-which contains an -OH group and can act as a  $\pi$ -type donor- and alcohol molecules, which have one acidic H atom on the -OH group and can act as  $\sigma$ -acceptors,<sup>[11]</sup>. Thermodynamic and transport properties of ternary mixtures of liquids have been studied employing the molar volume ratios of mixing, over entire composition range, at different temperatures, by various researchers.<sup>[3], [5], [7], [8]</sup>. In this paper densities ( $\rho$ ) and viscosities ( $\mu$ ) of ternary mixtures of water, methanol and ethanol covering an entire composition (expressed by volume fraction) at 308.15, 313.15, 318.15, 323.15, 328.15, K are reported. Excess volume ( $V^E$ ), excess viscosity ( $\mu^E$ ), and excess free energy of activation of viscous flow ( $\Delta G^E$ ) have been calculated from experimental values of densities and viscosities

## II. MATERIALS AND METHOD

An ethanol, and methanol (BDH grades, 99.4% v/v) and distilled water were used in the experiment. The viscometer was kept for 10 -15 minutes in the thermostatically controlled water-bath<sup>[6]</sup>, to achieve constant temperature. The measurements of flow time of the solution between the two points on the viscometer were performed at least three times for each liquid and the average results were noted. All liquids making up a mixture were of equal proportion by volume. The volumes of the particular mass of the liquid at different temperatures studied were noted. Then the densities of the liquids and liquid mixtures at different temperatures were calculated using the relation, density = mass/volume. The average of three readings of time of flow of each liquid or mixture at different temperatures was used in determining the corresponding viscosity.

The excess function is a measure of deviation from the ideal behaviour of the mixture, and found to be highly sensitive towards molecular interactions between the <sup>component</sup> molecules of liquid mixtures. The sign and magnitude of these excess functions from ideal depends on the strength of interaction between unlike molecule<sup>[7]</sup>.

The excess viscosity ( $\mu^E$ ) of the given binary liquid mixture was calculated from the observed viscosity of mixture and that of its pure components using following equation<sup>[1], [2]</sup>

$$\mu^E = \mu - (x_1\mu_1 + x_2\mu_2 + x_3\mu_3 + \dots + x_n\mu_n) \quad (1)$$

Where  $\mu$  is viscosity of ternary mixture,  $\mu_1, \mu_2, \mu_3, \dots, \mu_n$  are the viscosities of pure components respectively and  $x_1, x_2, x_3, \dots, x_n$  are the mole fractions of components of ternary liquid mixtures respectively.

The excess volume ( $V^E$ ) of ternary mixture can be evaluated from the volume of mixture ( $V$ ) and that of pure components ( $V_1, V_2, V_3, \dots, V_n$ )

$V^E$  can be determined using the following equation<sup>[12]</sup>.

$$V^E = V - (x_1V_1 + x_2V_2 + x_3V_3 + \dots + x_nV_n) \quad (2)$$

The volume  $V$  of the ternary liquid mixture can be calculated from the measured density ( $\rho$ ) of the mixture using following equation, (Glassstone, 1941).

$$V = (x_1V_1 + x_2V_2 + x_3V_3 + \dots + x_nV_n) / \rho \quad (3)$$

The excess Gibb's free energy of flow ( $\Delta G^E$ ) for the ternary liquid mixture was computed from the Eyring equation,

$$\Delta G^E = RT (\ln \mu V - x_1 \ln \mu_1 V_1 - x_2 \ln \mu_2 V_2 - x_3 \ln \mu_3 V_3 - \dots - x_n \ln \mu_n V_n) \quad (4)$$

### III. RESULTS AND DISCUSSION

Densities and viscosities of pure components from experimental values presented in Tables 1 and 2 respectively have been compared with the literature values and found that the experimental values are fairly comparable with values from literature.

**Table 1 Variation of densities, with temperatures for mixture, distilled water, methanol and water**

Temperature (K) $\pm 0.01$	Density (water) (g/cm <sup>3</sup> ) $\pm 0.005$	Density (methanol) (g/cm <sup>3</sup> ) $\pm 0.005$	Density (ethanol) (g/cm <sup>3</sup> ) $\pm 0.005$
308.15	0.994	0.726	0.777
313.15	0.992	0.719	0.773
318.15	0.990	0.711	0.769
323.15	0.988	0.704	0.765
328.15	0.985	0.696	0.762

**Table 2 Variation of viscosity coefficients with temperature for distilled water, methanol and water**

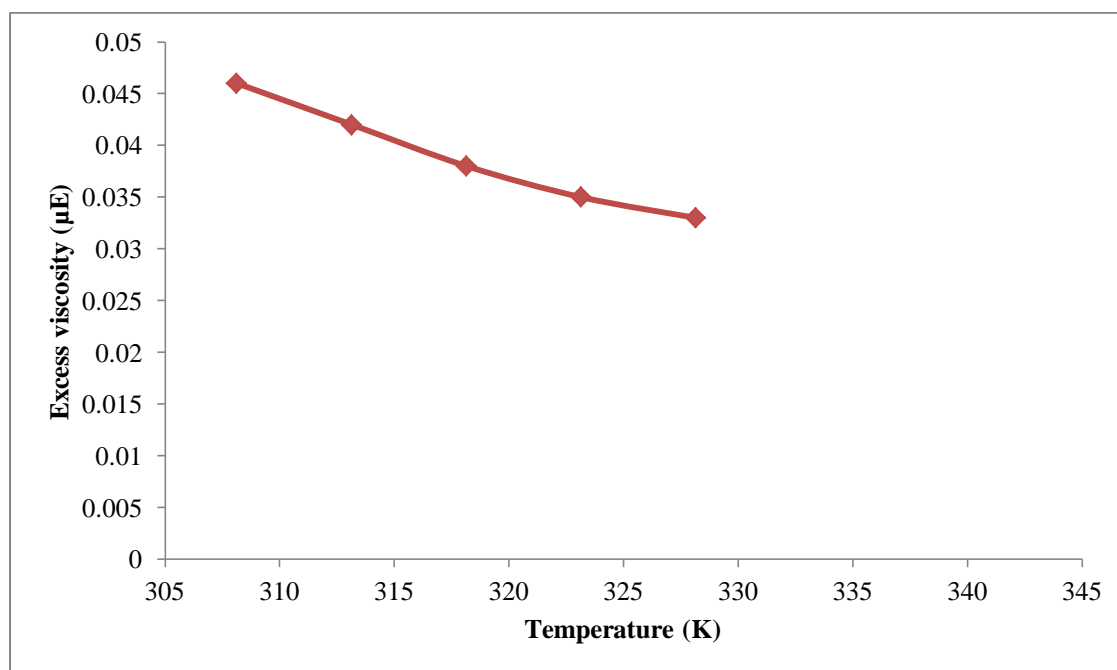
Temperaure (K) $\pm 0.01$	Viscosity ( $\mu$ ) of water (10 <sup>-4</sup> Pa.sec) $\pm 0.001$	Viscosity ( $\mu$ ) methanol (10 <sup>-4</sup> Pa.sec) $\pm 0.001$	Viscosity ( $\mu$ ) of ethanol (10 <sup>-4</sup> Pa.sec) $\pm 0.001$
308.15	7.220	4.831	9.083
313.15	6.526	4.556	8.324
318.15	5.959	4.292	7.632
323.15	5.564	4.031	7.005
328.15	5.038	3.848	6.421

The values of excess volume ( $V^E$ ), excess viscosity ( $\mu^E$ ), and excess Gibb's free energy of activation of low ( $\Delta G^E$ ), as a function of temperature of water-methanol- ethanol mixtures are presented in Table 3

**Table 3 Variation of  $\mu^E$ ,  $V^E$  and  $\Delta G^E$  with temperature**

Temperature (K) 0.01	Excess viscosity ( $\mu^E$ ) ( $10^{-4}$ Pa.sec)	Excess volume ( $V^E$ ) $\pm 0.005$	Excess Gibb's free energy of activation ( $\Delta G^E$ )
308.13	0.046	-0.646	114.76
313.15	0.042	-0.603	121.28
318.15	0.038	-0.575	126.22
323.15	0.035	-0.555	130.01
328.15	0.033	-0.550	133.14

From the plot of  $\mu^E$  versus T for mixture presented in the Fig 1 shows that the values of  $\mu^E$  are positive over entire experimental temperatures. The positive of  $\mu^E$  suggest that dispersion types of forces are predominant in these mixtures. Alcohols are associate liquids; they can interact with each other and with water molecules. For water-alcohol mixtures, the hydrogen bonding between water and alcohol molecules is much more predominant than for water-water, and alcohol-alcohol molecule pairs<sup>[11],[13]</sup>.



**Fig. 1 Variation of excess viscosity ( $\mu^E$ ) of water-methanol- ethanol mixture with temperature**

Fig 2 shows the plot of  $V^E$  of the mixture versus temperature T. The increase in temperature results in decrease in  $V^E$  of the mixture. The excess volumes are negative over entire experimental temperatures, indicating chemical or specific interactions which can result in decrease in volume due some molecular interactions. The hydrogen of the -OH group on alcohol is polar as it is in the water molecule. Also, in solvents such as alcohol, which can take part in hydrogen bond formation, the self-association of alcohols may be increased in favour of hydrogen - bonded forms between solute and solvent<sup>[11],[9]</sup>..

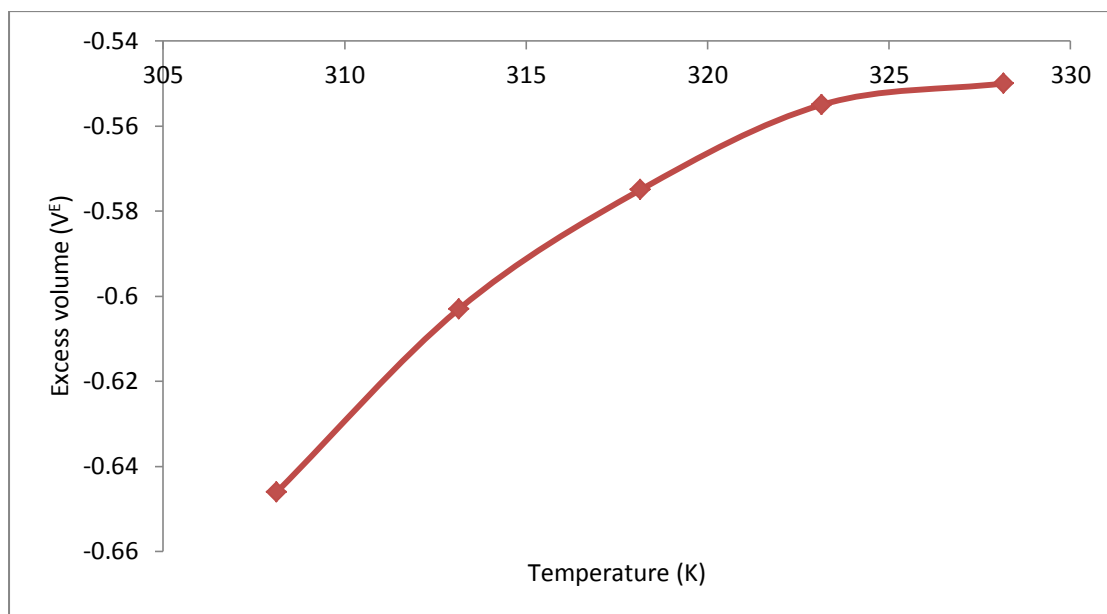


Fig. 2 Variation of excess volume ( $V^E$ ) of water-methanol- ethanol mixture with temperature

The values of  $\Delta G^E$  for the above mixture have been plotted against T represented in Fig 3. The positive values of  $\Delta G^E$  may be due to the size effect of the mixing components<sup>[9], [10]</sup>.  $\Delta G^E$  may be considered, a reliable measure to detect the presence of interaction between the molecule, positive values of  $\Delta G^E$  can be seen in ternary mixture where specific interactions (hydrogen bonding) between the molecules are dominant.

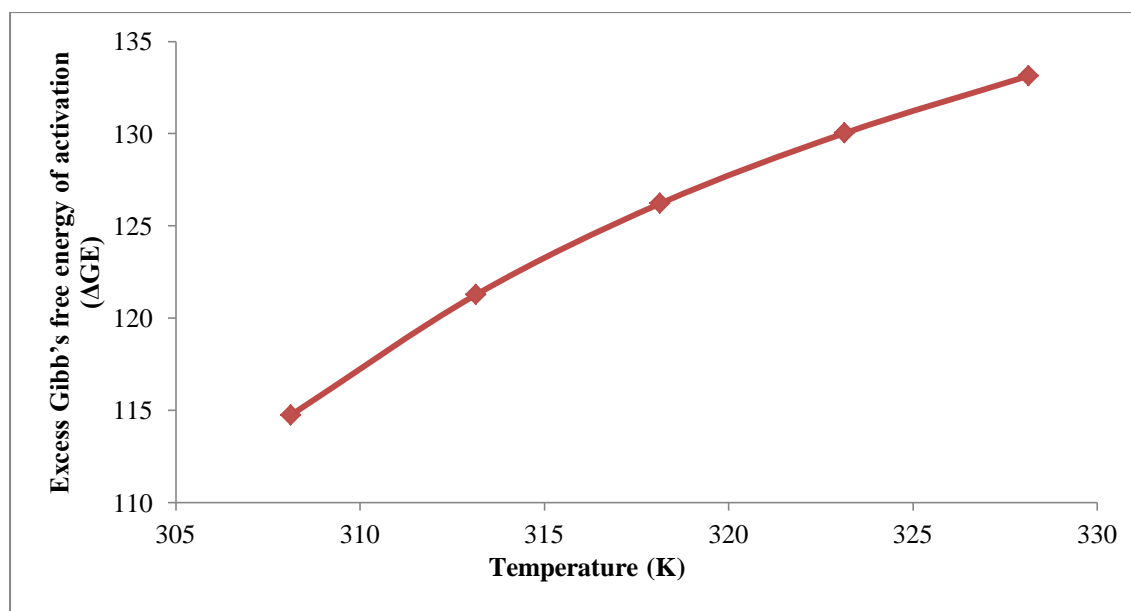


Fig. 3 Variation of Excess Gibbs's free energy of activation ( $\Delta G^E$ ) of water-methanol- ethanol mixture with temperature

For a strong hydrogen bond donor mixing cosolvents-specific donor-acceptor interactions may probably produce stable stoichiometric complexes which are formed in competition with the simultaneous disruption of the structures of both the pure solvents [2], [11], [13]. This behavior has been attributed to the fact that the O-H bond moment of these aggregates is increased through mutual induction. On the other hand, the H-bonded complexes of water present a dipole moment. Consequently, taking into account all these assumptions, we could attribute the observed deviations from ideality to all these effects.

#### IV. CONCLUSION

From the above results, the excess properties of the studied mixture indicate some molecular interactions. Because of alcohols are associate liquids, they can interact with each other and with water molecules. Viscosity, volume, Gibb's free energy of activation of flow parameters were affected from these interactions. The excess values of these components exhibited parabolic nature which means a deviation from ideal.

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