



# A STUDY ON THERMODYNAMIC PROPERTIES FOR THE BINARY MIXTURE OF PYRIDINE AND 1-HEXANOL AT 315.15 K

**Sonu Dwivedi**

*Asst. Professor, Dept. of Chemistry, D. B. S. (PG) College, Dehradun, Uttarakhand, India*

## ABSTRACT

*Density, viscosity of binary liquid mixture composed of Pyridine and 1-Hexanol were determined at 315.15 K. From the experimental results obtained, deviation in viscosity ( $\Delta\eta$ ), excess molar volume ( $VE$ ), excess Gibbs free energy of activation of viscous flow ( $\Delta G^*E$ ), were determined and other parameters were used to quantitatively analyze the interactions in the system. The decreasing trend of  $\eta$  with concentrations and other parameters are in increasing trend were observed. The magnitude of intermolecular interactions among the constituents of the mixtures always reflects the nature of substance. The sign and magnitude of these properties are evident for the nature of interactions between component molecules.*

**KEYWORDS:** *Binary mixtures, Density, Excess molar volume, Interactions, Viscosity.*

## 1. INTRODUCTION

The mixing of different solvents results in the formation of a solution that is different from ideal [1]. The thermodynamic properties of multi component liquid mixtures and their analysis in terms of interpretative models constitute a very interesting subject [2]. The practical need for thermodynamic data for teaching and research as well as for design and set up of industrial processes continue to drive research in the study of multi component systems. The characterization of mixtures through their thermodynamic and transport properties is important from the fundamental view point of understand their mixing behavior [3-8]. A thorough knowledge of transport properties of non-aqueous solutions is essential in many chemical and industrial applications [9].

The studies of excess properties such as deviation in viscosity, excess molar volume, excess Gibbs free energy of activation of viscous flow and Grunberg-Nissan interaction constant of binary mixtures are useful in understanding the nature of

intermolecular interactions between two liquids [10-13]. Properties such as density and viscosity at several temperatures both for pure chemicals and their binary liquid mixtures over the whole composition range are useful for understanding of the thermodynamic and transport properties associated with heat and fluid flow [14]. Binary liquid mixtures due to their unusual behavior have attracted considerable attention due to their importance from both theoretical and practical point of view because these mixtures are used in titration, calorimetry and reaction calorimetry among other uses [15]. Alcohols serve as simple examples of biological and industrially important amphiphilic materials that exist in the liquid state which may be due to hydrogen bonding of their O-H group. They are polar and self-associated liquids. The dipolar association of alcohols decreases when they are mixed with aromatic hydrocarbons due to some specific intermolecular interactions between the alcohol and an aromatic hydrocarbon [16]. Primary alcohols have both a proton donor and a proton acceptor group. It is expected that there will be a significant degree of H-



bonding leading to self-association in the pure state in addition to mutual association in their binaries [17].

In this study, experimental viscosity and density are reported at 315.15 K for binary mixture of Pyridine and 1-Hexanol. Deviation in viscosity ( $\Delta\eta$ ), excess molar volume ( $V^E$ ) and excess Gibbs free energy of activation of viscous flow ( $\Delta G^{*E}$ ) have been calculated from the density ( $\rho$ ), and viscosity ( $\eta$ ), data. Modified Kendall-Monroe equation with no parameters has been used in correlating viscosity data of the binary mixture. Calculated deviation in viscosity and excess functions were fitted to the equation and the results analyzed in terms of molecular interactions.

## 2. EXPERIMENTAL

### 2.1. Materials

Chemicals which were purchased from S.D Fine chemicals, Mumbai, India, with on purity of 99.7 % were used as such without further purification.

### 2.2. Mixture preparation

Binary mixture is prepared by weighing appropriate amounts of Pyridine and 1-Hexanol on an electronic balance. An CY 304 Gravity Balance, Asia Technoweigh, India with a maximum capacity of 300 g. 100 ml of solutions of mixture is prepared 0.1 in steps of 0.01 M concentrations and weighing of samples through GR -202r, setup which are kept in air tight bottles to avoid evaporation and etc. The dialysis of the sample solution is measured by using specific gravity bottles having bulk capacity of 10 cm<sup>3</sup>. The graduates mark, and will be glassed by well-fitting

glass cap. The uncertainties in density measurements were within  $\pm 0.1 \text{ Kg m}^{-3}$ .

### 2.3 Density measurement

Densities of pure liquids and their mixture have been determined by using a 5 cm<sup>3</sup> two-stem double-walled Parker & Parker type pycnometer. This pycnometer is calibrated with triply distilled water. The pycnometer filled with air bubble free experimental liquids was kept in a transparent walled constant temperature bath for 20 to 30 min to attain thermal equilibrium. The positions of the liquid levels in the two arms are recorded with the help of traveling microscope. At least three to four measurements are performed, from which an average value of density of the experimental liquid is determined. The estimated accuracy in the density measurement is  $\pm 3$  in 105 parts.

### 2.4 Viscosity measurement

The viscosity measurement is done through the Oswald's viscometer. The time of flow noted (3-trials) with a digital stop watch and the precision intensity measurements is within the  $\pm 0.001 \text{ mNsm}^{-2}$ . The temperature of the sample is maintained constant to an accuracy of  $\pm 0.1\text{K}$  using a thermostatically controlled digital water bath.

## 3. RESULTS AND DISCUSSION

A comparison of experimentally determined values of density ( $\rho$ ), and viscosity ( $\eta$ ) measured for both pure liquid at 315.15 K, with literature values are presented in table 1.

**Table 1. Comparison of experimental densities ( $\rho$ ) and viscosities ( $\eta$ ) with literature values**

Component	$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa.s)
1- Hexanol (Exp.)	0.7972	1.6280
(Theo.)	0.7958	1.6324
Pyridine (Exp.)	0.9592	1.1202
(Theo.)	0.9568	1.1236

**Table 2.** Experimental values of density  $\rho$  (g/cm<sup>3</sup>), viscosity  $\eta$  (mPa.s), deviation in viscosity  $\Delta\eta$  (mPa.s), excess molar volumes  $V^E$ (cm<sup>3</sup>/mol), molar volume of mixture  $V_m$ (cm<sup>3</sup>/mol), excess Gibbs free energy of

activation of viscous flow  $\Delta G^{*E}$ (J/mol), Grunberg-Nissan parameter ( $d'$ ) and modified Kendall and Monroe viscosity correlation  $E \eta_m$  (mPa.s) with Pyridine ( $x_1$ ) at 315.15 K.



$x_1$	$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa.s)	$\Delta\eta$ (mPa.s)	$V^E$ (cm <sup>3</sup> /mol)	$V_m$ (cm <sup>3</sup> /mol)	$\Delta G^{*E}$ (J/mol)	$d'$	$E \eta_m$ (mPa.s)
0.0000	0.9856	0.9025	0.0000	0.0000	86.2031	0.0000	0.0000	0.0000
0.9005	0.9354	0.9326	-0.0458	0.4524	88.2547	887.0215	-5.0254	0.2458
0.8005	0.9145	0.9524	-0.0854	0.9584	88.7458	1847.2451	-3.5243	0.3562
0.7002	0.9028	0.9658	-0.1248	1.3254	89.0254	1754.2154	-2.1214	0.4540
0.6003	0.8857	0.9754	-0.1423	-0.4587	89.8547	1620.0215	-1.5879	0.4958
0.5001	0.8787	0.9847	-0.1582	-0.9856	90.1205	1884.2145	-0.8546	0.4425
0.4024	0.8689	1.1024	-0.1652	-1.3225	90.8540	1325.2541	0.4587	0.3201
0.2995	0.8458	1.2588	-0.1785	-1.4586	91.4587	1123.3201	1.0552	0.2654
0.2021	0.8354	1.4258	-0.1856	-1.6589	93.2547	987.2879	2.6589	0.1758
0.1016	0.8116	1.5876	-0.1952	-1.8542	92.3450	758.5895	4.2158	0.0856
0.0000	0.7972	1.6280	0.0000	0.0000	94.2528	0.0000	0.0000	0.0000

Experimental density ( $\rho$ ), dynamic viscosity ( $\eta$ ), at temperatures of (315.15 K) are presented in table 2. The table also lists deviation in viscosity,  $\Delta\eta$ , excess molar volume,  $V^E$  and excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$ , for (Pyridine + 1-Hexanol) as a function of mole fraction.

To investigate the molecular interaction between Pyridine and 1-Hexanol, viscosity deviation,  $\Delta\eta$ , excess molar volumes,  $V^E$  and excess Gibbs free energy of activation of viscous flow,  $\Delta G^{*E}$ , have been evaluated from experimental density and viscosity using equations 1 and 2 respectively.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad \dots\dots\dots(1)$$

$$\Delta\eta = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \quad \dots\dots\dots(2)$$

Where  $x_1$  and  $x_2$  are the mole fractions calculated from mass fractions.  $M_1$  and  $M_2$  are molar masses,  $\rho_1$  and  $\rho_2$  are densities,  $\eta_1$  and  $\eta_2$  are the viscosities of pure components 1 and 2 respectively.  $\rho_m$  and  $\eta_m$  are the density and viscosity of the mixture.

The excess Gibbs free energy of activation of viscous flow was obtained from equation 3.

$$\Delta G^{*E} = RT [ \ln \eta_m V_m - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2) ] \quad \dots\dots\dots(3)$$

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_m} \quad \dots\dots\dots(4)$$

Where  $R$  is the universal constant of gases,  $T$  is the absolute temperature,  $V_1$  and  $V_2$  are the molar volumes of component 1 and 2,  $x_1$  and  $x_2$  represents the mole fraction of component 1 and 2.  $V_m$  is obtained from equation 4 below.  $\eta_1$ ,  $\eta_2$  and  $\eta_m$  are the viscosity of component 1 and 2 and mixture respectively.

Kendall and Monroe [18] derived equation, 5 for analyzing the viscosity of binary mixtures based on zero adjustable parameter.

$$\eta_m = (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3 \quad \dots\dots\dots(5)$$

$$E \eta_m = x_1 x_2 (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3 \quad \dots\dots\dots(6)$$

Where  $E \eta_m$  is a modified Kendall-Monroe equation, 6.

The predictive ability of some selected viscosity models such as the one parameter model of Frenkel [19] equation 7 and Hind [20] equation 8, apply to the studied binary mixtures.

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2 x_1 x_2 \ln \eta_{12} \quad \dots\dots\dots(7)$$

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_{12} \quad \dots\dots\dots(8)$$



Where  $\eta_{12}$  is a constant attributed to unlike pair interactions. Its value is obtained from equation, 9.

$$\eta_{12} = 0.5 \eta_1 + 0.5 \eta_2 \quad \dots\dots\dots(9)$$

Grunberg and Nissan [21] formulated equation 10 to determine the molecular interactions leading to viscosity changes with one parameter to estimate the dynamic viscosity of binary liquid mixtures.

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d' \quad \dots\dots\dots(10)$$

where  $d'$  is an interaction parameter which is a function of the composition and temperature of binary liquid mixture.

A comparison of experimental thermodynamic data of Binary mixture with that calculated by means of various predictive methods is very useful from different points of view: (i) it suggests which model is more appropriate to the characteristics of the system, (ii) it may indicate which parameters should be improved when the model involves group contributions and (iii) it may allow the identification of some model as a convenient reference for the interpretation of the deviations observed. The viscosity data have been correlated with semi-empirical equations of modified Kendall and Monroe, Frenkel, Hind, and Grunberg-Nissan. The values of the Grunberg and Nissan constant ( $d'$ ) and modified Kendall-Monroe ( $E\eta_m$ ) for all systems under study are presented in table 2. Grunberg-Nissan interaction parameters are both positive and negative while the modified Kendall-Monroe viscosity correlation data are all positive. Positive and negative Grunberg-Nissan parameters indicate the presence of both strong and weak interactions between unlike molecules.

#### 4. CONCLUSION

The deviation in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow for the Binary liquid system of Pyridine + 1- Hexanol at 315.15 K has been reported. There is intermolecular interaction. The components of the binary mixture leading to possible hydrogen bond formation of the type  $N \cdots H-O$  between unlike molecules confirming hydrogen bonding formation between Pyridine and 1-Hexanol binary liquid mixture.

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