# EXCESS THERMODYNAMIC PROPERTIES OF A BINARY LIQUID MIXTURE OF ISOPROPYLBENZENE AND *N*, *N*-DIMETHYLFORMAMIDE AT T= 293.15 K, 303.15 K AND 313.15 K

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Abstract: Excess molar volume, viscosity and refractive index of binary mixture of Isopropylbenzene and *N*, *N*-Dimethylformamide (DMF) have been experimentally measured at atmospheric pressure and three different temperatures (293.15 K, 303.15 K, and 313.15 K) over the entire composition range. The experimental data were then used to compute density ( $\rho$ ), deviation in viscosity ( $\Delta \eta$ ), deviation in molar refraction ( $\Delta R$ ) and excess Gibbs energy of activation ( $G^E$ ) as a function of composition. The experimental viscosity data were correlated using Grunberg and Nissan equation, Herric's Correlation and three body McAllister equation. The excess thermodynamic properties were fitted to the Redlich-Kister equation to obtain the coefficients and standard deviations. The variation of these properties with composition and temperature are discussed in terms of intermolecular interactions.

## *Index Terms*: Isopropylbenzene, *N*, *N*-dimethylformamide, excess Gibbs energy of activation, excess molar volume.

## I. INTRODUCTION

The investigation of excess thermodynamic properties of binary liquid mixture provides important and useful information focused on intermolecular interactions in liquids and their mixtures. Such volumetric data are significant for formulating models and theories of solutions and testing the reliability of the existing methods for prediction of the system behavior. The knowledge of thermodynamic properties of liquid mixtures is important in all chemical engineering applications, especially in design of various separation equipments. The degree of non-ideality which is due to the presence of several secondary binding forces can be well judged by the respective excess thermodynamic properties. When two or more solvent molecules are associated with one another in a liquid mixture, it brings about a marked effect on the properties of the resulting system. Volumetric properties of liquid mixtures are an important source of information for the characterization of the interactions between components.

*N*, *N*-Dimethylformamide (DMF) is an industrial solvent used widely in a variety of industrial processes like in the manufacture of synthetic fibers, leathers, films, and in the surface coatings. DMF is a stable, highly polar and non-aqueous compound representative of amidic solvent. DMF as pure solvent is certainly to some extent associated by means of dipole–dipole interactions, and is of particular interest because any significant structural effects are absent due to the lack of hydrogen bonds; therefore it may work as an aprotic protophilic solvent of large dipole moment and high dielectric constant ( $\mu$ = 3.24 Debye and  $\varepsilon$  = 36.71 at 298.15 K). Due to a better hydrogen bond acceptor ability of the oxygen atom in DMF, it can interact with non-polar Isopropylbenzene and makes structural effects and packing effects. These properties allow DMF to dissolve polar and non-polar liquids. DMF finds applications in polymer science and pharmaceutical industry. In addition, it can serve as a model compound of peptides to obtain information on protein systems. Isopropylbenzene is a constituent of crude oil and refined fuels. It is a flammable colorless liquid with a gasoline-like odor. It is insoluble in water, but is soluble in many organic solvents, such as ethanol and benzene.

# II. RESEARCH METHODOLOGY

## 2.1 Chemicals used

Isopropyl benzene (AR grade, Sigma-Aldrich, China) and *N*, *N*–Dimethylformamide (AR grade, Merck Specialities Pvt. Ltd., Mumbai) were used in the study after purification. The chemicals used were first purified using standard procedures <sup>[1]</sup> and stored over molecular sieves. Then the chemicals were further purified by fractional distillation method as done by Gill et al.<sup>[2]</sup>. The purity of the chemicals was checked by comparing the measured refractive indices and viscosities with the reported literature values. The data are presented in Table 1.

#### 2.2 Apparatus and procedure

V-shaped dilatometer was used to measure excess molar volume of binary mixture over the entire composition range. The dilatometer's capillary was calibrated from the weight of mercury column in the capillary. The length of the mercury column in capillary at various positions was read by a travelling microscope that could read to  $\pm 0.001$ cm.

Excess molar volumes,  $V^E$  for binary mixtures were then calculated from the expression:

$$V^E = \frac{\pi r^2 \Delta h}{(n_1 + n_2)}$$

where,  $\Delta h$  is the change in height of liquid level in capillary before and after mixing and  $n_1, n_2$  are the number of moles of liquid A and B respectively.

Modified Ubbelohde viscometer was used to measure viscosity of pure chemicals and binary mixture. Viscometer was calibrated using distilled benzene and cyclohexane at three different temperatures and thus, constants A and B of the following equation <sup>[3]</sup> were calculated.

## $\eta/\rho = At + B/t$

where, v, kinematic viscosity =  $\eta/\rho$ , t=average time and A, B are constants.

The viscometer was washed with water several times and then with acetone before each reading. The viscometer is finally dried under vacuum. The required temperature of the sample was maintained constant by circulating-type cryostat (type MK70, MLW, Germany). The Cryostat consist of a long reservoir i.e. (container contains water) of water where the temperature was maintained or regulated by electronic controller. The estimated uncertainties in the measurements of temperature were 0.02 K.

Equilibrated mixtures were analyzed by the Refractive Index method using a Bausch and Lomb Abbe-3L refractometer. Refractive index readings were taken on samples with sufficient time allowed for the sample to come to thermal equilibrium at 298.15 K with the help of a circulating type cryostat (Type MK70, MLW, Germany) maintained at a temperature with in  $\pm$  0.02 K. The refractometer was calibrated by using a distilled water (whose R.I=1.333) at 20<sup>o</sup>C and by using benzene and cyclohexane.

## III. DATA TREATMENT AND CORRELATIONS USED

Table 2, table 3 and table 4 display the experimentally measured values of viscosity, excess volume, and refractive index as well as calculated data on density, deviation in Molar Refraction, deviation in Viscosity and Excess Gibbs Energy of Activation for the binary mixture of Isopropyl benzene + N, N-Dimethylformamide over the entire composition range at 293.15 K, 303.15K and 313.15K respectively.

The density of the binary mixture was calculated from the excess molar volume data by the following relation:

$$\rho_{\rm m} = \frac{(M_1 x_1 + M_2 x_2)}{(V^{\rm E} + x_1 V_1^0 + x_2 V_2^0)} \tag{3.1}$$

where,  $V^{\rm E}$  is the excess molar volume,

 $x_1$  and  $x_2$  are mole fractions,  $M_1$  and  $M_2$  are molecular masses and  $V_1^0$  and  $V_2^0$  are molar volumes of pure components 1 & 2 respectively.

The deviation in viscosity was obtained by the following equation:

$$\Delta \eta = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \tag{3.2}$$

where,  $\eta_1$  and  $\eta_2$  are the viscosities of pure components 1 & 2 respectively and  $\eta_m$  is the mixture viscosity. Molar Refraction R<sub>m</sub>, was calculated by using the experimentally determined values of refractive index with the help of Lorentz-Lorenz equation:

$$\mathbf{R}_{\mathbf{m}} = \frac{[\mathbf{n}_{\mathbf{D}}^2 - \mathbf{1}]}{[\mathbf{n}_{\mathbf{D}}^2 + \mathbf{2}]} \cdot \frac{\sum \mathbf{x}_i \mathbf{M}_i}{\mathbf{o}_{\mathbf{m}}}$$
(3.3)

The deviation in molar refraction is calculated with the help of following relation:

$$\Delta \boldsymbol{R} = \boldsymbol{R}_m - \sum \boldsymbol{x}_i \, \boldsymbol{R}_i \tag{3.4}$$

where,  $\Delta R$  is the deviation in molar refraction,  $R_m$  is the molar refraction of mixture, and  $R_i$  is the molar refraction of pure component.

The excess Gibbs free energy of activation of binary mixture can be calculated using the relation:

$$\frac{G^E}{RT} = \ln(\eta V_m) - \sum_{i=1}^2 x_i \ln(\eta_i V_i)$$
(3.5)

where,  $G^{E}$  is excess Gibbs energy of activation, R is universal gas constant, T is temperature in Kelvin,  $V_1$  and  $V_2$  are the molar volumes of the pure components 1 and 2 and  $V_m$  is the molar volume of the mixture.

The excess molar volume ( $V^{E}$ ), excess Gibbs energy of activation ( $G^{E}$ ), deviation in molar refraction ( $\Delta R$ ) and deviation in viscosity ( $\Delta \eta$ ) were fitted to Redlich-Kister type equation <sup>[5]</sup>:

$$A = x_1 x_2 \sum_{j=1}^{n} A_{j-1} (x_1 - x_2)^{j-1}$$
(3.6)

where, A is the property under consideration,  $A_{j-1}$  is the polynomial coefficient and n is the polynomial degree, and  $x_1$ ,  $x_2$  refers to the mole fractions.

The standard deviation in each case can be calculated using Standard deviation equation <sup>[6]</sup>:

$$\boldsymbol{\sigma}(\boldsymbol{X}) = \left[\frac{\Sigma(X_{exp} - X_{cal})^2}{N - n}\right]^{1/2}$$
(3.7)

where, X is the property under consideration,  $X_{exp}$ ,  $X_{cal}$  are the experimental and calculated values respectively, N is the number of data points and n is the number of coefficients.

Coefficients (A<sub>K</sub>) of the Redlich-Kister Equation and Standard Deviations ( $\sigma$ ) are listed in table 5. The experimentally determined values of viscosity were fitted to McAllister model <sup>[7]</sup> given by:

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3 x_1^2 x_2 \ln A_{12} + 3 x_1 x_2^2 \ln A_{21} - \ln \left[ x_1 + x_2 \frac{M_2}{M_1} \right] + 3 x_1^2 x_2 \ln \left[ \frac{2 + (M_2/M_1)}{3} \right] \\ + 3 x_1 x_2^2 \ln \left[ \frac{1 + (2M_2/M_1)}{3} \right] + x_2^3 \ln \left[ \frac{M_2}{M_1} \right]$$

where,  $v_1, v_2$  are the kinematic viscosity values of mixture and pure component respectively.  $x_1, x_2$  refers to the mole fractions and  $M_1, M_2$  are the molecular weights of pure components 1 and 2 respectively.  $A_{12}, A_{21}$  are the parameters. Kinematic viscosities were fitted to Herric's Correlation<sup>[8]</sup> and the parameters were determined.

$$ln\nu = x_1 ln\nu_1 + x_2 ln\nu_2 + x_1 x_2 [\alpha_{12} + \alpha'_{12}(x_1 - x_2)] - lnM_{mix} + x_1 lnM_1 + x_2 lnM_2$$

where,  $v_1, v_2$  are the kinematic viscosity values of mixture and pure component respectively.  $x_1, x_2$  refers to the mole fractions and M<sub>1</sub>, M<sub>2</sub> are the molecular weights of pure components 1 and 2 respectively.  $\alpha_{12}$  and  $\alpha_{21}$  are coefficients of Herric's correlation.

Grunberg and Nissan equation <sup>[9]</sup> was used to assess the molecular interactions leading to viscosity changes.

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d$$

where,  $\eta$  is the viscosity of mixture;  $\eta_1$  and  $\eta_2$  are the viscosity of pure components 1 and 2 respectively;  $x_1$ ,  $x_2$  refers to the mole fractions of pure components 1 and 2 respectively; *d* is the parameter which is a measure of the strength of the interaction between components of the binary mixture.

Table 6, 7 and 8 present the evaluated interaction parameters of McAllister model, Herric's correlation and Grunberg –Nissan parameter respectively.

Table 1 Comparison of experimental and literature values <sup>[4]</sup> of refractive index and viscosity

for the pure components at 293.15 K

| Component              | T (K)  |        |        | η (cP) |       |  |
|------------------------|--------|--------|--------|--------|-------|--|
|                        |        | Exp.   | Lit.   | Exp.   | Lit.  |  |
| Isopropylbenzene       | 293.15 | 1.4910 | 1.4915 | 0.7832 | 0.791 |  |
| N, N-Dimethylformamide | 293.15 | 1.4300 | 1.4305 | 0.8796 | 0.920 |  |

Table 2

Excess Molar Volume ( $V^{E}$ ), Density( $\rho$ ), Viscosity( $\eta$ ), Refractive Index( $n_{D}$ ), Deviation in Molar Refraction ( $\Delta R$ ), Deviation in Viscosity ( $\Delta \eta$ ) and Excess Gibbs Energy of Activation ( $G^{E}$ ) as a function of mole fraction of Isopropylbenzene ( $x_{1}$ ) at 293.15K

| <i>x</i> 1 | V <sup>E</sup><br>(cm <sup>3</sup> mole <sup>-1</sup> ) | ρ<br>(gcm <sup>-3</sup> ) | η<br>(cP) | n <sub>D</sub> | Δ <i>R</i><br>(cm <sup>3</sup> mol <sup>-1</sup> ) | Δη<br>(cP) | G <sup>E</sup><br>(J.mole <sup>-1</sup> ) |
|------------|---|---------------------------|-----------|----------------|--|------------|---|
| 0.0000     | 0.0000  | 0.9487                    | 0.8796    | 1.4300         | 0.0000   | 0.0000     | 0.0000                                    |
| 0.0569     | -0.0472   | 0.9407                    | 0.8691    | 1.4355         | -0.0290  | -0.0050    | 12.9204                                   |

| 0.1171 | -0.0976 | 0.9329 | 0.8603 | 1.4405 | -0.0733 | -0.0080 | 27.8924 |
|--------|---------|--------|--------|--------|---------|---------|---------|
| 0.1527 | -0.1247 | 0.9286 | 0.8533 | 1.4434 | -0.0933 | -0.0116 | 29.2534 |
| 0.2611 | -0.1878 | 0.9166 | 0.8407 | 1.4516 | -0.1410 | -0.0137 | 48.8174 |
| 0.3535 | -0.2202 | 0.9074 | 0.8308 | 1.4579 | -0.1662 | -0.0147 | 58.1615 |
| 0.4417 | -0.2427 | 0.8996 | 0.8221 | 1.4637 | -0.1696 | -0.0149 | 61.1934 |
| 0.5430 | -0.2445 | 0.8913 | 0.8131 | 1.4698 | -0.1565 | -0.0142 | 59.8716 |
| 0.6783 | -0.2037 | 0.8813 | 0.8024 | 1.4772 | -0.1141 | -0.0118 | 50.1711 |
| 0.7524 | -0.1773 | 0.8763 | 0.7979 | 1.4807 | -0.0953 | -0.0092 | 43.7627 |
| 0.8379 | -0.1378 | 0.8710 | 0.7916 | 1.4846 | -0.0638 | -0.0072 | 28.5252 |
| 0.9217 | -0.0814 | 0.8661 | 0.7872 | 1.4880 | -0.0364 | -0.0035 | 15.1694 |
| 1.0000 | 0.0000  | 0.8617 | 0.7832 | 1.4910 | 0.0000  | 0.0000  | 0.0000  |

Excess Molar Volume ( $V^{E}$ ), Density ( $\rho$ ), Viscosity ( $\eta$ ), Refractive Index ( $n_{D}$ ), Deviation in Molar Refraction ( $\Delta R$ ), Deviation in Viscosity ( $\Delta \eta$ ) and Excess Gibbs Energy of Activation ( $G^{E}$ ) as a function of mole fraction of Isopropylbenzene ( $x_{1}$ ) at 303.15K

| <i>x</i> 1 | V <sup>E</sup><br>(cm <sup>3</sup> mole <sup>-1</sup> ) | ρ<br>(gcm <sup>-3</sup> ) | η<br>(cP) | n <sub>D</sub> | Δ <i>R</i><br>(cm <sup>3</sup> mol <sup>-1</sup> ) | Δη<br>(cP) | G <sup>E</sup><br>(J.mole <sup>-1</sup> ) |
|------------|---|---------------------------|-----------|----------------|--|------------|---|
| 0.0000     | 0.0000  | 0.9412                    | 0.7640    | 1.4262         | 0.0000   | 0.0000     | 0.0000                                    |
| 0.0569     | -0.0401   | 0.9329                    | 0.7561    | 1.4318         | -0.0239  | -0.0035    | 16.6959                                   |
| 0.1171     | -0.0840   | 0.9249                    | 0.7496    | 1.4369         | -0.0646  | -0.0053    | 34.9728                                   |
| 0.1527     | -0.1088   | 0.9205                    | 0.7448    | 1.4398         | -0.0850  | -0.0074    | 40.0816                                   |
| 0.2611     | -0.1729   | 0.9083                    | 0.7338    | 1.4480         | -0.1358  | -0.0100    | 57.8801                                   |

| 0.3535 | -0.2067 | 0.8990 | 0.7263 | 1.4545 | -0.1543 | -0.0104 | 69.2321 |
|--------|---------|--------|--------|--------|---------|---------|---------|
| 0.4417 | -0.2216 | 0.8909 | 0.7186 | 1.4602 | -0.1584 | -0.0113 | 70.4281 |
| 0.5430 | -0.2195 | 0.8825 | 0.7119 | 1.4664 | -0.1411 | -0.0101 | 70.6544 |
| 0.6783 | -0.1918 | 0.8724 | 0.7037 | 1.4737 | -0.1065 | -0.0079 | 61.3026 |
| 0.7524 | -0.1623 | 0.8674 | 0.6997 | 1.4772 | -0.0908 | -0.0061 | 52.3935 |
| 0.8379 | -0.1271 | 0.8621 | 0.6943 | 1.4811 | -0.0625 | -0.0049 | 34.6662 |
| 0.9217 | -0.0743 | 0.8571 | 0.6903 | 1.4845 | -0.0338 | -0.0025 | 18.2534 |
| 1.0000 | 0.0000  | 0.8527 | 0.6867 | 1.4875 | 0.0000  | 0.0000  | 0.0000  |

Excess Molar Volume ( $V^{E}$ ), Density ( $\rho$ ), Viscosity ( $\eta$ ), Refractive Index ( $n_{D}$ ), Deviation in Molar Refraction ( $\Delta R$ ), Deviation in Viscosity ( $\Delta \eta$ ) and Excess Gibbs Energy of Activation ( $G^{E}$ ) as a function of mole fraction of Isopropylbenzene ( $x_{1}$ ) at 313.15K

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| <i>x</i> <sub>1</sub> | V <sup>E</sup><br>(cm <sup>3</sup> mole <sup>-1</sup> ) | ρ<br>(gcm <sup>-3</sup> ) | η<br>(cP) | n <sub>D</sub> | Δ <i>R</i><br>(cm <sup>3</sup> mol <sup>-1</sup> ) | Δη<br>(cP) | G <sup>E</sup><br>(J.mole <sup>-1</sup> ) |
|-----------------------|---|---------------------------|-----------|----------------|--|------------|---|
| 0.0000                | 0.0000  | 0.9310                    | 0.6766    | 1.4217         | 0.0000   | 0.0000     | 0.0000                                    |
| 0.0569                | -0.0314   | 0.9229                    | 0.6697    | 1.4274         | -0.0219  | -0.0030    | 17.6371                                   |
| 0.1171                | -0.0714   | 0.9152                    | 0.6641    | 1.4327         | -0.0588  | -0.0045    | 36.8694                                   |
| 0.1527                | -0.0952   | 0.9109                    | 0.6610    | 1.4357         | -0.0759  | -0.0052    | 46.7408                                   |
| 0.2611                | -0.1573   | 0.8991                    | 0.6515    | 1.4442         | -0.1189  | -0.0072    | 66.0074                                   |
| 0.3535                | -0.1906   | 0.8901                    | 0.6441    | 1.4507         | -0.1424  | -0.0083    | 74.6678                                   |
| 0.4417                | -0.2051   | 0.8823                    | 0.6375    | 1.4565         | -0.1476  | -0.0089    | 76.6944                                   |

| 0.5430 | -0.2068 | 0.8742 | 0.6317 | 1.4629 | -0.1256 | -0.0078 | 77.4505 |
|--------|---------|--------|--------|--------|---------|---------|---------|
| 0.6783 | -0.1812 | 0.8645 | 0.6238 | 1.4701 | -0.1077 | -0.0064 | 65.0458 |
| 0.7524 | -0.1551 | 0.8596 | 0.6193 | 1.4738 | -0.0815 | -0.0058 | 52.0940 |
| 0.8379 | -0.1148 | 0.8544 | 0.6148 | 1.4777 | -0.0551 | -0.0045 | 34.9925 |
| 0.9217 | -0.0617 | 0.8496 | 0.6113 | 1.4811 | -0.0332 | -0.0023 | 18.5267 |
| 1.0000 | 0.0000  | 0.8454 | 0.6082 | 1.4842 | 0.0000  | 0.0000  | 0.0000  |

Coefficients (A<sub>K</sub>) of the Redlich-Kister Equation and Standard Deviations ( $\sigma$ ) for least square representation of Excess Molar Volume ( $V^{E}$ ),Deviation in Molar Refraction( $\Delta R$ ), Deviation in Viscosity ( $\Delta \eta$ ) and Excess Gibbs Energy of Activation ( $G^{E}$ ) at 293.15K, 303.15K and 313.15K.

| EXCESS<br>PROPERTY                                   | T(K)   | A        | A        | A <sub>2</sub> | A <sub>3</sub> | σ       |
|--|--------|----------|----------|----------------|----------------|---------|
|  | 293.15 | -0.96081 | 0.10446  | -0.06181       | -0.32379       | 0.00439 |
| V <sup>E</sup> (cm <sup>3</sup> mole <sup>-1</sup> ) | 303.15 | -0.88760 | 0.09314  | -0.01056       | -0.34078       | 0.00142 |
|  | 313.15 | -0.84151 | 0.03037  | 0.11929        | -0.23428       | 0.00180 |
|  | 293.15 | -0.65163 | 0.353198 | 0.12045        | -0.40221       | 0.00300 |
| $\Delta R \ (\mathrm{cm}^3\mathrm{mol}^{-1})$        | 303.15 | -0.60849 | 0.33600  | 0.12369        | -0.42833       | 0.00308 |
|  | 313.15 | -0.56031 | 0.27476  | 0.12349        | -0.35243       | 0.00442 |
| Δη (cP)  | 293.15 | -0.06448 | -0.00816 | 0.03178        | 0.10471        | 0.00260 |

|  | 303.15 | -0.04175 | 0.01689  | -0.00646 | -0.00278 | 0.00042 |
|--|--------|----------|----------|----------|----------|---------|
|  | 313.15 | -0.03266 | 0.00796  | -0.00953 | 0.00067  | 0.00037 |
|  | 293.15 | 0.24601  | -0.01997 | -0.02894 | -0.00780 | 0.00169 |
| G <sup>E</sup> (kJ.mol <sup>-1</sup> ) | 303.15 | 028895   | -0.02342 | -0.00051 | -0.02899 | 0.00141 |
|  | 313.15 | 0.31384  | -0.06066 | -0.01524 | 0.00129  | 0.00156 |

Interaction parameters of the McAllister Model and its standard deviation ( $\sigma$ ) at 293.15, 303.15 and 313.15K

| T(K)   | A <sub>12</sub> | A <sub>21</sub> | σ       |
|--------|-----------------|-----------------|---------|
| 293.15 | 0.91850         | 0.92749         | 0.00062 |
| 303.15 | 0.81358         | 0.82121         | 0.00041 |
| 313.15 | 0.72644         | 0.73784         | 0.00035 |

Table 7

Interaction parameters of Herric's Correlation and its standard deviation ( $\sigma$ ) at 293.15, 303.15 and 313.15K

| T(K)   | a <sub>12</sub> | a <sub>21</sub> | σ       |
|--------|-----------------|-----------------|---------|
| 293.15 | 0.09820         | -0.00912        | 0.00062 |
| 303.15 | 0.11462         | -0.01447        | 0.00041 |
| 313.15 | 0.11918         | -002278         | 0.00035 |

| T(K)   | d        | σ       |
|--------|----------|---------|
| 293.15 | -0.06882 | 0.00147 |
| 303.15 | -0.05464 | 0.00104 |
| 313.15 | -0.04913 | 0.00060 |

Table 8Grunberg-Nissan parameter and its standard deviation ( $\sigma$ ) at 293.15, 303.15 and 313.15K

## IV. RESULTS AND DISCUSSION

Figure 1 reveals that the experimental V<sup>E</sup> values are negative over the entire composition range for the binary mixture of Isopropylbenzene and *N*, *N*–Dimethylformamide at the three selected temperatures i.e. 293.15 K, 303.15 K and 313.15 K. The negative values of V<sup>E</sup> indicate that there is a volume contraction on mixing. When two components mix, two effects, viz. the molecular interaction and the molecular stack, are combined together to enhance the volume contraction. As DMF molecule is polar with dipole moment of 3.86 D and Isopropylbenzene molecule is weakly polar with dipole moment of 0.65 D <sup>[10]</sup>, there may be some moderate interaction of the dipole with introduced-dipole between DMF and Isopropylbenzene. Main cause of volume contraction may arise from the large difference between the molar volumes of the two components i.e. 139.48 cm<sup>3</sup>mol<sup>-1</sup> for Isopropylbenzene and 77.04 cm<sup>3</sup>mol<sup>-1</sup> for DMF, as well as the difference between their molecular configurations (aliphatic for DMF and aromatic for Isopropylbenzene). These two effects cause the volume contraction <sup>[11]</sup>. Nikam and Kharat <sup>[12]</sup> suggested that the structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume. In other words, structural contributions arising from geometrical fitting (interstitially accommodated) of one component into another due to the differences in the free volume and molar volume between components lead to a negative contribution to V<sup>E</sup>. With increase in temperature, the kinetic energy of molecules increases, hence the contraction in volume decreases, and as a result V<sup>E</sup> increases <sup>[13]</sup>.

Experimental results show that with increase in temperature and composition of Isopropylbenzene, the viscosity of mixture decreases. From Fig. 2, it is observed that for the binary mixture of Isopropylbenzene and *N*, *N*– Dimethylformamide, viscosity deviations are negative, but with very small magnitude over the whole range of composition at all temperatures and value of  $\Delta \eta$  increases (becomes less negative) with increasing temperature. The negative deviation indicates presence of dispersion forces or weak dipole-dipole interactions between unlike components of the binary mixture <sup>[14]</sup>. For the three empirical correlations used for correlating viscosity, small standard deviation values (Table 6, 7 and 8) indicate the suitability of these equations to represent the viscosity of the binary mixture.

From Fig. 3, it is observed that  $\Delta R$  values are negative over the entire range of composition. Excess Gibbs energy of activation,  $G^{E}$  may be considered as a reliable measure to detect the presence of interaction between molecules. Positive values of  $G^{E}$  for the entire composition of Isopropylbenzene (1) + *DMF* (2) indicate specific interactions (dipole–dipole) between the molecules. The values of Excess Gibbs Energy of Activation increase with temperature which is evident from Fig. 4.



**Fig.1:** Excess Molar Volume ( $V^{E}$ ) vs. mole fraction of Isopropylbenzene ( $x_1$ ) at 293.15( $\blacklozenge$ ), 303.15K ( $\blacksquare$ ) and 308.15 K ( $\blacktriangle$ )



**Fig.2:** Deviation in Viscosity ( $\Delta \eta$ ) vs. mole fraction of Isopropylbenzene ( $x_1$ ) at 293.15( $\blacklozenge$ ), 303.15K ( $\blacksquare$ ) and 308.15 K ( $\blacktriangle$ )



**Fig.3:** Deviation in Molar refraction ( $\Delta R$ ) vs. mole fraction of Isopropylbenzene ( $x_1$ ) at 293.15( $\blacklozenge$ ), 303.15K ( $\blacksquare$ ) and 308.15 K( $\blacktriangle$ )



**Fig.4:** Excess Gibbs Energy of Activation ( $G^E$ ) vs. mole fraction of Isopropylbenzene ( $x_1$ ) at 293.15( $\blacklozenge$ ), 303.15K ( $\blacksquare$ ) and 308.15 K ( $\blacktriangle$ )

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