

## Viscometric Studies of Binary Mixtures of Ethyl Acetoacetate with (C<sub>4</sub>-C<sub>9</sub>) Aliphatic Ketones at 298.15 K

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Kinematic viscosities ( $\nu$ ) of binary mixtures of ethyl acetoacetate (EAA) + aliphatic ketones (C<sub>4</sub>-C<sub>9</sub>) have been determined as a function of composition at 298.15 K. The dynamic viscosity ( $\eta$ ), excess viscosity and excess Gibbs free energy of activation for viscous flow, ( $\Delta G^{\text{E}}$ ) were also calculated. Excess viscosities ( $\eta^{\text{E}}$ ) and excess Gibbs free energies of activation for viscous flow ( $\Delta G^{\text{E}}$ ) were calculated from the experimental viscosity data and were fitted to a Redlich-Kister type polynomial. The excess viscosity shows negative deviations over the entire range of solvents composition for the mixtures of (ethyl acetoacetate) + butan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one and a positive deviation for the binary mixtures of ethyl acetoacetate + pentan-2-one system. The ( $\Delta G^{\text{E}}$ ) were all positive over the entire range solvents composition for the binary mixtures. The experimental results were used to test some semi-empirical equations to correlate viscosity-composition data.

**Keywords:** Binary mixtures, Intermolecular interactions, Excess viscosities, Activation energies.

### INTRODUCTION

Knowledge of the viscosity of binary mixtures is of great importance in many industrial processes. It is rare to determine the viscosity of the mixtures from the sum of the viscosities of pure components [1]. Theoretical study of the viscosity of mixtures is generally complicated. Thermodynamic and transport properties of liquid-liquid mixtures have been used to understand the molecular interactions between the components of mixture and for engineering applications [2].

In this paper, we report an experimental measurements of the viscosities, dynamic viscosity ( $\eta$ ) of ethyl acetoacetate with butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one and those of their binary mixtures with ethyl acetoacetate as common solvent at 298.15 K covering the whole composition range of the solvent systems expressed by mole fraction,  $X_1$  of ethyl acetoacetate. This is part of our research [3,4] on the accumulation of the data of binary organic liquid mixtures. The aim of the present studies is to improve our understanding of the intermolecular interactions of these solvent systems in order to characterize their physico-chemical

behaviour in their mixtures. The density data for the same systems were reported earlier [4].

The viscosities and excess viscosities of binary liquid mixtures of ethyl acetoacetate with butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one at 298.15 K as a function of composition were reported. The values of excess viscosities have been fitted to the Redlich-Kister polynomial equation [5] to derive the binary coefficients and estimate the standard deviations between the experimental and calculated results. Furthermore, the viscosities of these binary mixtures were calculated theoretically from the pure component data by using various semi-empirical relations of Frenkel [6], Hind *et al.* [7], Grunberg & Nissan [8] and Kendall & Monroe [9]. In addition, excess Gibbs free energies of activation for viscous flow ( $\Delta G^{\text{E}}$ ) have been calculated for the binaries of ethyl acetoacetate with butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one at the same temperature range. To our best of knowledge there is no work on the viscosity data of ethyl acetoacetate (EAA) and the (C<sub>4</sub>-C<sub>9</sub>) aliphatic ketones reported in the literature for these solvent systems.

## EXPERIMENTAL

The reagents ethyl acetoacetate, butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one obtained from Acros Organics, Belgium were of analytical grade and used without further purification. The densities of pure solvents were determined according to earlier publication [4]. Varying mole fractions of mixtures ranging in composition from 0.0000 to 1.0000 mole fraction of ethyl acetoacetate were prepared as previously described [4]. The purities of solvents were checked by comparing the experimental values of densities and viscosities with those reported in the literature [10-13] at 298.15 K (Table-1).

Kinematic viscosity ( $\nu$ ) and dynamic viscosity ( $\eta$ ) determinations were carried out using Anton Paar SVM 3000 Stabinger Viscometer. The viscometer has a dynamic viscosity range of 0.2 to 20 000 mPa.s, a kinematic viscosity range of 0.2 to 20000 mm<sup>2</sup>/s and a density range of 0.65 to 3 g/cm<sup>3</sup>. The instrument is equipped with a maximum temperature range of +105 °C and a minimum of 20 °C below ambient. Instrument viscosity reproducibility is 0.35 % of measured value and density reproducibility of 0.0005 g/cm<sup>3</sup>.

## RESULTS AND DISCUSSION

The experimental values of pure viscosities ( $\eta$ ) are reported in Table-1 together with literature values for comparison. No experimental data of viscosities were found for the studied mixtures with ethyl acetoacetate at 298.15K, with which a comparison of the present viscosity values could be made.

From the viscosity and density measurements, excess viscosities ( $\eta^E$ ) and excess Gibbs free energies of activation for viscous flow ( $\Delta G^{*E}$ ), were calculated for the binary mixtures using the eqns. 1 and 2, respectively.

$$\eta^E = \eta_m - (x_1\eta_1 - x_2\eta_2) \quad (1)$$

where, in eqns. 1 and 2,  $x_1$  is mole fraction of ethyl acetoacetate;  $x_2$  is mole fraction of aliphatic ketone;  $\eta_1$ ,  $\eta_2$  and  $\eta_m$  are viscosities of ethyl acetoacetate, aliphatic ketones and of the mixture (mPa.s) respectively and

$$\Delta G^{*E} = RT[\ln \eta_m V_m - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (2)$$

where R is gas constant, T is absolute temperature in Kelvin and  $V_1$ ,  $V_2$  and  $V_m$  are the molar masses of ethyl acetoacetate, aliphatic ketone and mixture (g mol<sup>-1</sup>), respectively.

The dependence of excess viscosities ( $\eta^E$ ) and excess Gibbs free energies of activation for viscous flow ( $G^{*E}$ ) on mole fraction was fitted into the Redlich-Kister [5] polynomial (eqn. 3).

$$Y^E = x(1-x) \sum_{i=0}^n A_i (2x-1)^i \quad (3)$$

$$Y^E = x_1 x_2 [A_0 + A_1 (2x_1 - 1)^1 + A_2 (2x_1 - 1)^2 + A_3 (2x_1 - 1)^3 + A_4 (2x_1 - 1)^4] \quad (4)$$

where  $Y^E$  represents  $\eta^E$  or  $\Delta G^{*E}$ ,  $x$  denotes the mole fraction of ethyl acetoacetate,  $n$  is the number of coefficients and  $A_i$  are the fitting coefficients. The method of least-square was used to determine the values of coefficients  $A_i$ . The optimum number of these coefficients in each case was ascertained from the standard deviations ( $\sigma Y^E$ ), of the estimate with  $n$  of the systems defined by eqn. 5:

$$\sigma Y^E = \sqrt{\frac{\sum (Y_{\text{expt}}^E - Y_{\text{calcd}}^E)^2}{m - n}} \quad (5)$$

In eqn. 5,  $m$  is the number of experimental  $Y^E$  data points and  $n$  is the number of coefficients,  $Y_{\text{expt}}^E$  and  $Y_{\text{calcd}}^E$  are experimental and calculated  $\eta^E$  and  $\Delta G^{*E}$ , respectively. The  $n$  value was considered to be 4 in this present calculation. The experimental results obtained for the binary systems are listed in Tables 2-4. The values of the parameter,  $A_i$ , along with the standard deviations are given in Tables 5 and 6 for the studied binary mixtures.

Fig. 1 shows the variation with the composition of excess viscosity,  $\eta^E$  values for the binary mixtures of EAA + butan-2-one, EAA + pentan-2-one, EAA + hexan-2-one, EAA + heptan-2-one, EAA + octan-2-one and EAA + nonan-2-one, respectively at the studied temperature. Excess viscosities ( $\eta^E$ ) values are negative over the entire solvents composition range for the systems EAA + butan-2-one, EAA + hexan-2-one, EAA + heptan-2-one, EAA + octan-2-one and EAA + nonan-2-one. The negative excess viscosities ( $\eta^E$ ) values are generally observed for the systems where dispersion of weak dipole-dipole forces of interaction between the component molecules are primarily responsible [14,15].

On mixing, ethyl acetoacetate being more polar will induce a dipole moment in the ketone molecule, which might lead to a weak dipole-induced dipole interaction between the component molecules. Negative deviation in viscosities,  $\eta^E$ , was also being observed due to the differences in molecular size of component molecules [16-18] as in the present binary mixtures. The magnitude of negative values of excess viscosities,  $\eta^E$  (Fig. 1) follows the sequence; butan-2-one > heptan-2-one > nonan-2-one > octan-2-one > hexan-2-one.

A close look at Fig. 1 revealed that  $\eta^E$  values for the binary mixtures of EAA + pentan-2-one is completely positive while

TABLE-1  
COMPARISON OF EXPERIMENTAL AND LITERATURE VALUES OF  
DENSITY ( $\rho$ ) AND VISCOSITY ( $\eta$ ) OF PURE SOLVENTS AT 298.15 K

| Solvents           | Acronym | $\rho$ (g/cm <sup>3</sup> ) |                            | $\eta$ (mPa.s) |                                     |
|--------------------|---------|-----------------------------|----------------------------|----------------|-------------------------------------|
|                    |         | Exp.                        | Lit.                       | Exp.           | Lit.                                |
| Butan-2-one        | 2-BUT   | 0.7997                      | 0.79970 [12], 0.79960 [13] | 0.3760         | 0.3835 [10], 0.378 [11], 0.381 [12] |
| Pentan-2-one       | 2-PENT  | 0.8017                      | 0.80150 [14]               | 0.4625         | 0.461 [10], 0.438 [11]              |
| Hexan-2-one        | 2-HEX   | 0.8073                      | 0.80725 [12,13]            | 0.6193         |                                     |
| Heptan-2-one       | 2-HEP   | 0.8105                      | 0.81050 [12,13]            | 0.7684         | 0.77 [12]                           |
| Octan-2-one        | 2-OCT   | 0.8157                      | 0.81520 [12]               | 0.9687         |                                     |
| Nonan-2-one        | 2-NON   | 0.8175                      | 0.81730 [12]               | 1.1771         |                                     |
| Ethyl acetoacetate | EAA     | 1.0216                      | 1.02160 [12,13]            | 1.1473         |                                     |

TABLE-2  
DYNAMIC VISCOSITIES,  $\eta$  (mPa.s) OF BINARY MIXTURES OF ETHYL  
ACETOACETATE (EAA) AND ( $C_4 - C_6$ ) ALIPHATIC KETONES AT 298.15 K

| $x_1$  | $\eta$ (mPa.s) |              |             |              |             |             |
|--------|----------------|--------------|-------------|--------------|-------------|-------------|
|        | Butan-2-one    | Pentan-2-one | Hexan-2-one | Heptan-2-one | Octan-2-one | Nonan-2-one |
| 0.0000 | 0.3760         | 0.4625       | 0.6193      | 0.7684       | 0.9687      | 1.1771      |
| 0.1152 | 0.4951         | 0.5756       | 0.6788      | 0.8089       | 0.9794      | 1.1700      |
| 0.2047 | 0.5440         | 0.6255       | 0.7283      | 0.8355       | 0.9841      | 1.1228      |
| 0.3106 | 0.6130         | 0.6815       | 0.7575      | 0.8658       | 1.0006      | 1.1470      |
| 0.4115 | 0.6913         | 0.7431       | 0.8128      | 0.9074       | 1.0158      | 1.1446      |
| 0.5038 | 0.7618         | 0.8122       | 0.8664      | 0.9447       | 1.0396      | 1.1504      |
| 0.6047 | 0.8202         | 0.8601       | 0.9297      | 0.9891       | 1.0665      | 1.1546      |
| 0.7006 | 0.9226         | 0.9699       | 0.9971      | 1.0393       | 1.0964      | 1.1650      |
| 0.8027 | 0.9830         | 1.0471       | 1.0687      | 1.0910       | 1.1347      | 1.1796      |
| 0.9015 | 1.0947         | 1.1378       | 1.1066      | 1.1609       | 1.1794      | 1.2024      |
| 1.0000 | 1.2309         | 1.2309       | 1.2309      | 1.2309       | 1.2309      | 1.2309      |

TABLE-3  
EXCESS VISCOSITIES,  $\eta^E$  (mPa.s) OF BINARY MIXTURES OF ETHYL  
ACETOACETATE AND ( $C_4 - C_6$ ) ALIPHATIC KETONES AT 298.15 K

| $x_1$  | $\eta^E$ (mPa.s) |              |             |              |             |             |
|--------|------------------|--------------|-------------|--------------|-------------|-------------|
|        | Butan-2-one      | Pentan-2-one | Hexan-2-one | Heptan-2-one | Octan-2-one | Nonan-2-one |
| 0.0000 | 0.0000           | 0.0000       | 0.0000      | 0.0000       | 0.0000      | 0.0000      |
| 0.1152 | -0.0151          | 0.0292       | 0.0017      | -0.0091      | -0.0047     | -0.0057     |
| 0.2047 | -0.0231          | 0.0466       | 0.0014      | -0.0145      | -0.0078     | -0.0092     |
| 0.3106 | -0.0287          | 0.0613       | -0.0007     | -0.0191      | -0.0108     | -0.0122     |
| 0.4115 | -0.0306          | 0.0693       | -0.0022     | -0.0216      | -0.0128     | -0.0139     |
| 0.5038 | -0.0299          | 0.0715       | -0.0043     | -0.0223      | -0.0138     | -0.0145     |
| 0.6047 | -0.0268          | 0.0684       | -0.0063     | -0.0213      | -0.0137     | -0.0140     |
| 0.7006 | -0.0221          | 0.0600       | -0.0073     | -0.0187      | -0.0126     | -0.0124     |
| 0.8027 | -0.0155          | 0.0453       | -0.0069     | -0.0141      | -0.0098     | -0.0095     |
| 0.9015 | -0.0080          | 0.0254       | -0.0047     | -0.0079      | -0.0057     | -0.0054     |
| 1.0000 | 0.0000           | 0.0000       | 0.0000      | 0.0000       | 0.0000      | 0.0000      |

TABLE-4  
EXCESS GIBBS FREE ENERGIES OF ACTIVATION FOR VISCOUS FLOW ( $J mol^{-1}$ ) OF BINARY  
MIXTURES OF ETHYL ACETOACETATE AND ( $C_4 - C_6$ ) ALIPHATIC KETONES AT 298.15 K

| $x_1$  | $G^{*E}$ ( $J mol^{-1}$ ) |              |             |              |             |             |
|--------|---------------------------|--------------|-------------|--------------|-------------|-------------|
|        | Butan-2-one               | Pentan-2-one | Hexan-2-one | Heptan-2-one | Octan-2-one | Nonan-2-one |
| 0.0000 | 0.0000                    | 0.0000       | 0.0000      | 0.0000       | 0.0000      | 0.0000      |
| 0.1152 | 0.5177                    | 0.4632       | 0.4077      | 0.3408       | 0.3812      | 0.3802      |
| 0.2047 | 0.8148                    | 0.7294       | 0.6495      | 0.5453       | 0.6051      | 0.6039      |
| 0.3106 | 1.0527                    | 0.9433       | 0.8515      | 0.7185       | 0.7902      | 0.7890      |
| 0.4115 | 1.1702                    | 1.0495       | 0.9601      | 0.8141       | 0.8874      | 0.8867      |
| 0.5038 | 1.1886                    | 1.0670       | 0.9883      | 0.8418       | 0.9102      | 0.9099      |
| 0.6047 | 1.1164                    | 1.0032       | 0.9422      | 0.8063       | 0.8642      | 0.8645      |
| 0.7006 | 0.9628                    | 0.8660       | 0.8243      | 0.7087       | 0.7533      | 0.7539      |
| 0.8027 | 0.7135                    | 0.6424       | 0.6205      | 0.5361       | 0.5646      | 0.5655      |
| 0.9015 | 0.3927                    | 0.3539       | 0.3468      | 0.3011       | 0.3143      | 0.3150      |
| 1.0000 | 0.0000                    | 0.0000       | 0.0000      | 0.0000       | 0.0000      | 0.0000      |

TABLE-5  
COEFFICIENTS OF REDLICH-KISTER EQUATION AND STANDARD DEVIATION VALUES FOR  
 $\eta^E$  (mPa.s) OF THE BINARY MIXTURES OF EAA AND ( $C_4 - C_6$ ) ALIPHATIC KETONES AT 298.15 K

| Solvents                         | $A_0$   | $A_1$   | $A_2$  | $A_3$  | $\sigma(Y^E)$ |
|----------------------------------|---------|---------|--------|--------|---------------|
| Butan-2-one [ $\eta^E$ (mPa.s)]  | -0.1383 | -0.0615 | 0.027  | -0.025 | 0.427         |
| Pentan-2-one [ $\eta^E$ (mPa.s)] | -0.1483 | 0.6253  | 0.041  | 0.047  | 0.550         |
| Hexan-2-one [ $\eta^E$ (mPa.s)]  | -0.1016 | 0.0731  | -0.014 | -0.007 | 0.338         |
| Heptan-2-one [ $\eta^E$ (mPa.s)] | -0.1483 | -0.0083 | 0.013  | 0.015  | 0.317         |
| Octan-2-one [ $\eta^E$ (mPa.s)]  | -0.1116 | 0.0199  | 0.069  | 0.007  | 0.271         |
| Nonan-2-one [ $\eta^E$ (mPa.s)]  | -0.1016 | 0.0049  | 0.013  | 0.013  | 0.226         |

TABLE-6  
COEFFICIENTS OF REDLICH-KISTER EQUATION AND STANDARD DEVIATION VALUES FOR  
 $G^{*E}$  (J mol<sup>-1</sup>) OF THE BINARY MIXTURES OF EAA AND (C<sub>4</sub> – C<sub>6</sub>) ALIPHATIC KETONES AT 298.15 K

| Solvents                                | A <sub>0</sub> | A <sub>1</sub> | A <sub>2</sub> | A <sub>3</sub> | $\sigma(Y^E)$ |
|-----------------------------------------|----------------|----------------|----------------|----------------|---------------|
| Butan-2-one [ $\Delta G^{*E}$ (J/mol)]  | 7.2346         | 0.6948         | -1.337         | -0.011         | 14.17         |
| Pentan-2-one [ $\Delta G^{*E}$ (J/mol)] | 6.4912         | 0.0997         | 5.838          | 0.085          | 13.57         |
| Hexan-2-one [ $\Delta G^{*E}$ (J/mol)]  | 6.5278         | 0.5900         | 0.101          | 0.228          | 12.85         |
| Heptan-2-one [ $\Delta G^{*E}$ (J/mol)] | 5.6627         | -0.0498        | 0.237          | -0.036         | 12.07         |
| Octan-2-one [ $\Delta G^{*E}$ (J/mol)]  | 5.8594         | 0.2111         | -0.011         | -0.086         | 12.06         |
| Nonan-2-one [ $\Delta G^{*E}$ (J/mol)]  | 5.8760         | 0.1928         | 0.592          | 0.067          | 12.12         |

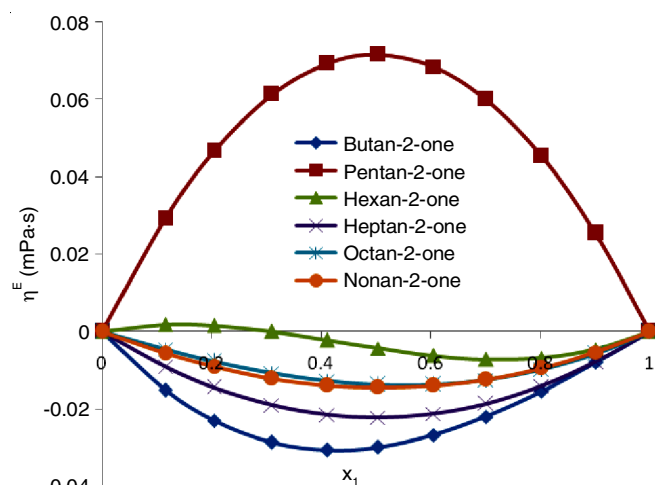


Fig. 1. Plots of excess viscosities of EAA + butan-2-one (1), + pentan-2-one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 298.15 K

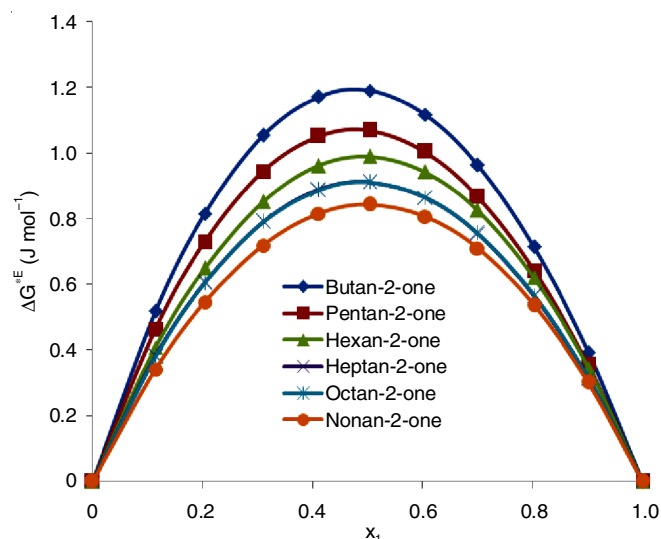


Fig. 2. Plots of excess Gibbs free energy of EAA + butan-2-one (1), + pentan-2-one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 298.15 K

for EAA with hexan-2-one, the  $\eta^E$  values are positive at lower EAA rich region and negative at higher EAA rich region. The positive excess viscosities,  $\eta^E$ , values are indicative of specific interactions [19-21], while the negative excess viscosities ( $\eta^E$ ) values indicate that dispersion forces are dominant. Furthermore, the existence of dispersion forces indicates that component molecules have different molecular size and shape [22,23].

The magnitude of the negative deviation of  $\eta^E$  decreases as the chain length increase; this suggests that the strength of interaction between unlike molecules become weaker as chain length increases [24]. Fig. 1 shows that the values of  $\eta^E$  for hexan-2-one at lower EAA rich region for EAA + hexan-2-one binary mixtures was positive, the small positive values of excess viscosity at lower concentrations of EAA indicates that the interactions at that mole fraction regions was very weak. The interactions between EAA and pentan-2-one show large positive values of excess viscosity which also revealed that there were weak interactions between the solvent systems. The positive excess viscosities ( $\eta^E$ ) suggest that specific interactions were present in the mixtures [25-27]. The positive  $\eta^E$  observed in pentan-2-one and at lower EAA rich region of hexan-2-one systems imply that the mixture was more viscous than the corresponding ideal mixture at specified interactions.

The values of  $\Delta G^{*E}$  (Fig. 2) for binary mixtures of EAA + butan-2-one, EAA + pentan-2-one, EAA + hexan-2-one, EAA + heptan-2-one, EAA + octan-2-one and EAA + nonan-2-one are completely positive over the entire range of solvent composition. The positive values of excess Gibbs free energy of activation for viscous flow  $\Delta G^{*E}$  decrease with increase in

chain length of the aliphatic ketones. As suggested by Ciocirlan and Iulian [28] large negative values of excess Gibbs free energies of activation for viscous flow indicates the presence of weak interactions, whereas large positive values of excess Gibbs free energies of activation for viscous flow suggest specific association between the molecules in the binary mixtures, *i.e.* there are stronger interactions between unlike molecules than those between like molecules in the binary mixed solvent systems.

Gowrisankar *et al.* [11], Singh & Diwedi [29] and Prakash *et al.* [30] have explained the behaviour of solvent mixtures based upon the sign and magnitude of the values of excess Gibbs free energies of activation for viscous flow and excess viscosities. According to these researchers, the positive values of  $\Delta G^{*E}$  are indicative of strong interactions while negative values indicate weak interactions between unlike molecules. Thus, the authors suggested that positive values of  $\Delta G^{*E}$  indicate that the flow of binary mixtures is more difficult when compared to that of pure solvents. The observed positive values of  $\Delta G^{*E}$  in the binary mixtures of EAA + butan-2-one, EAA + pentan-2-one, EAA + hexan-2-one, EAA + heptan-2-one, EAA + octan-2-one and EAA + nonan-2-one are indicative of strong dipole-dipole interactions between ethyl acetoacetate molecules and the named aliphatic ketones. Leal *et al.* [31,32] made similar observations in their studies of binary mixtures of pyrrolidin-2-one with (C<sub>6</sub>-C<sub>10</sub>) alkan-1-ols.

The positive values of  $\eta^E$  and  $\Delta G^{*E}$  suggests that the strength of specific interaction was not the only factor, but the molecular



sizes and shapes of the components were equally an important factor that affected the behaviour of the systems. The negative  $\eta^E$  values indicated that dispersion or weak dipole-dipole forces were dominant; furthermore, the existence of dispersion forces suggests that the component molecules have different molecular sizes and shapes [21]. Molecules were interstitially fitted in which the lower molecular structures were accommodated by the larger molecular structures. The negative values of  $\eta^E$  supported the main factor of breaking of self-associated and weak interactions between unlike molecules [33]. This was observed for the systems of EAA + butan-2-one, EAA + heptan-2-one, EAA + octan-2-one and EAA + nonan-2-one. The negative  $\eta^E$  values were generally observed for the systems where dispersion or weak dipole-dipole forces primarily responsible for the interaction between the component molecules. The negative  $\eta^E$  may also be observed due to the difference in the molecular size of component molecules as in the present mixtures. The magnitude of negative  $\eta^E$  values (Fig. 1) followed the sequence: butan-2-one > heptan-2-one > nonan-2-one > octan-2-one > hexan-2-one.

**Correlating models for mixture viscosities:** To describe the viscosity of binary mixtures, the experimental viscosities of binary mixtures of ethyl acetoacetate (EAA) with (C<sub>4</sub>-C<sub>9</sub>) aliphatic ketones at 298.15 K were fitted to different expressions existing in the literature for correlation, the following equations relating viscosities of binary mixtures as a function of those of the pure components were selected:

The Grunberg and Nissan [8] model was based on Arrhenius equation for dynamic viscosity of mixed solvent:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d' \quad (6)$$

where  $d'$  is an adjustable parameter which is independent of the mixture composition and represents a measure of the intermolecular interactions between unlike molecules. Frenkel [6] derived the following equation:

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

and Hind *et al.* [7] proposed the following relationship as:

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

where  $\eta_{12}$  is Frenkel & Hind interaction parameter and is independent of the composition, which was obtained from the relation:

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

Kendall and Monroe [9] model was used for analyzing the viscosity of binary mixtures based on zero adjustable parameter as:

$$\eta_m = (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3 \quad (10)$$

$$E\eta_m = x_1 x_2 (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3 \quad (11)$$

where  $E\eta_m$  is a modified Kendall-Monroe equation.

All the fitting parameters of eqns. 6, 7, 8 and 11 were deduced from experimental data by non-linear least squares methods. The correlating ability of these models was tested by calculating Average Standard Deviation (APD) between experimental and calculated viscosity as:

$$APD = \frac{100}{N} \sum_{i=1}^N \left[ \frac{\eta_{\text{exptal}} - \eta_{\text{calcd}}}{\eta_{\text{exptal}}} \right] \quad (12)$$

where  $\eta_{\text{expt}}$  and  $\eta_{\text{calcd}}$  represent the viscosity of experimental and calculated data,  $N$  is the number of experimental data points in each set and  $i$  the number of numerical coefficients in the equations,  $Y$  indicates the respective correlating property.

Table-7 shows the results obtained for the correlation parameters. A close examination of these values revealed that the magnitude of values of Frenkel, Hind and Kendall-Monroe correlations are positive over the entire range of solvents composition, but Grunberg-Nissan correlation values are both positive and negative over the entire range of solvents composition for butan-2-one and hexan-2-one solvent systems, entirely positive for pentan-2-one solvent system and show negative throughout the entire solvent composition range for heptan-2-one, octan-2-one and nonan-2-one systems (Figs. 3-6). Several researchers [10,34-36] reported that positive values of Grunberg-Nissan, Hind and Tamura-Kurata adjustable parameters indicate the presence of specific interactions and negative values suggests the presence of weak interactions between the unlike molecules of mixture. The positive values observed in this work for Frenkel,

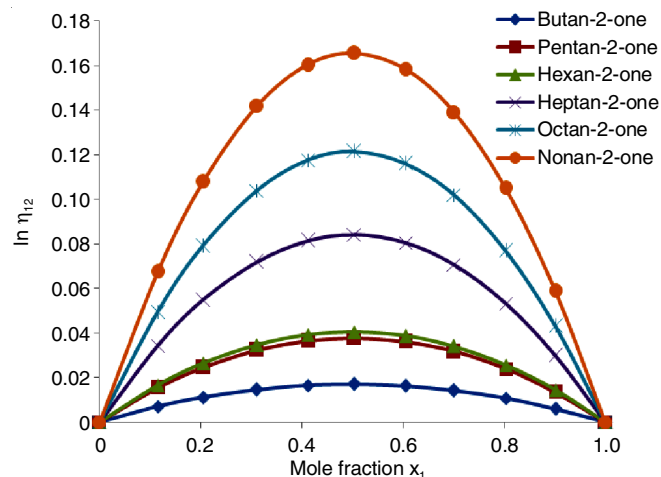


Fig. 3. Plots of Frenkel correlation ( $\ln \eta_{12}$ ) of EAA + butan-2-one (1), + pentan-2-one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 298.15 K

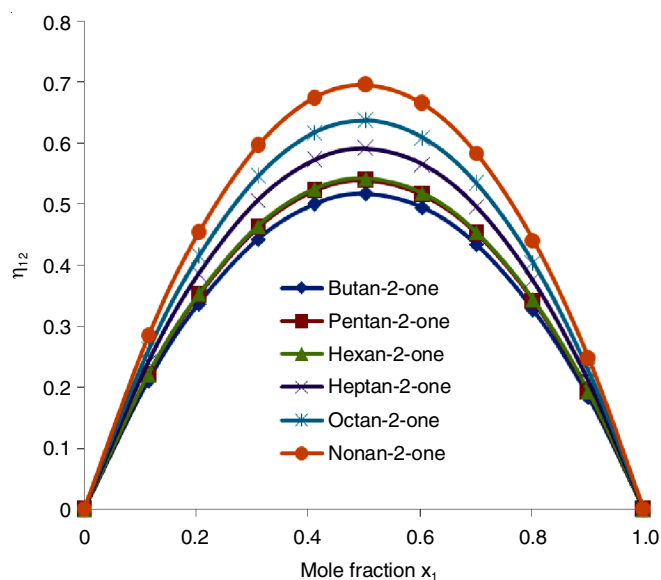


Fig. 4. Plots of Hind correlation ( $\eta_{12}$ ) of EAA + butan-2-one (1), + pentan-2-one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 298.15 K

TABLE-7  
VISCOSITY DATA CORRELATION PARAMETERS [FRENKEL ( $\ln \eta_{12}$ ), HIND ( $\eta_{12}$ ), GRUNBERG-NISSAN ( $d'$ ) AND KENDALL-MONROE ( $E\eta_m$ )] OF BINARY MIXTURES OF ETHYL ACETOACETATE AND KETONE SOLVENT SYSTEMS AT 298.15 K

| $x_1$                                     | $\ln \eta_{12}$ | $\eta_{12}$ | $d'$    | $E\eta_m$ (mPa.s) | $\ln \eta_{12}$                           | $\eta_{12}$ | $d'$    | $E\eta_m$ (mPa.s) |
|-------------------------------------------|-----------------|-------------|---------|-------------------|-------------------------------------------|-------------|---------|-------------------|
| Ethyl acetoacetate (1) + Butan-2-one (2)  |                 |             |         |                   | Ethyl acetoacetate (1) + Heptan-2-one (2) |             |         |                   |
| 0.0000                                    | 0.0000          | 0.0000      | 0.0000  | 0.0000            | 0.0000                                    | 0.0000      | 0.0000  | 0.0000            |
| 0.1152                                    | 0.0154          | 0.2198      | 0.7602  | 0.0457            | 0.0343                                    | 0.2411      | -0.5172 | 0.0859            |
| 0.2047                                    | 0.0245          | 0.3511      | 0.4384  | 0.0869            | 0.0547                                    | 0.3852      | -0.3309 | 0.1474            |
| 0.3106                                    | 0.0323          | 0.4618      | 0.3064  | 0.1388            | 0.0719                                    | 0.5066      | -0.3231 | 0.2105            |
| 0.4115                                    | 0.0365          | 0.5222      | 0.2524  | 0.1866            | 0.0814                                    | 0.5729      | -0.2459 | 0.2569            |
| 0.5038                                    | 0.0376          | 0.5391      | 0.2013  | 0.2239            | 0.0840                                    | 0.5915      | -0.2398 | 0.2839            |
| 0.6047                                    | 0.0360          | 0.5155      | -0.0242 | 0.2503            | 0.0803                                    | 0.5656      | -0.2329 | 0.2919            |
| 0.7006                                    | 0.0316          | 0.4524      | -0.0303 | 0.2529            | 0.0705                                    | 0.4963      | -0.2262 | 0.2741            |
| 0.8027                                    | 0.0238          | 0.3415      | -0.5194 | 0.2204            | 0.0532                                    | 0.3747      | -0.2556 | 0.2220            |
| 0.9015                                    | 0.0134          | 0.1915      | -1.2444 | 0.1411            | 0.0298                                    | 0.2101      | -0.2029 | 0.1330            |
| 1.0000                                    | 0.0000          | 0.0000      | 0.0000  | 0.0000            | 0.0000                                    | 0.0000      | 0.0000  | 0.0000            |
| Ethyl acetoacetate (1) + Pentan-2-one (2) |                 |             |         |                   | Ethyl acetoacetate (1) + Octan-2-one (2)  |             |         |                   |
| 0.0000                                    | 0.0000          | 0.0000      | 0.0000  | 0.0000            | 0.0000                                    | 0.0000      | 0.0000  | 0.0000            |
| 0.1152                                    | 0.0069          | 0.2109      | 0.0093  | 0.0568            | 0.0495                                    | 0.2599      | -0.2722 | 0.1034            |
| 0.2047                                    | 0.0111          | 0.3368      | 0.1043  | 0.1028            | 0.0790                                    | 0.4151      | -0.2626 | 0.1735            |
| 0.3106                                    | 0.0145          | 0.4431      | 0.0384  | 0.1558            | 0.1039                                    | 0.5459      | -0.2281 | 0.2416            |
| 0.4115                                    | 0.0165          | 0.5011      | 0.0545  | 0.2004            | 0.1176                                    | 0.6174      | -0.2814 | 0.2883            |
| 0.5038                                    | 0.0169          | 0.5172      | 0.1178  | 0.2317            | 0.1214                                    | 0.6373      | -0.2529 | 0.3123            |
| 0.6047                                    | 0.0162          | 0.4946      | 0.0204  | 0.2496            | 0.1161                                    | 0.6094      | -0.2689 | 0.3145            |
| 0.7006                                    | 0.0142          | 0.4340      | 0.1821  | 0.2442            | 0.1018                                    | 0.5348      | -0.2692 | 0.2897            |
| 0.8027                                    | 0.0108          | 0.3277      | 0.1159  | 0.2062            | 0.0769                                    | 0.4038      | -0.2734 | 0.2301            |
| 0.9015                                    | 0.0060          | 0.1837      | 0.1539  | 0.1284            | 0.0431                                    | 0.2264      | -0.2557 | 0.1354            |
| 1.0000                                    | 0.0000          | 0.0000      | 0.0000  | 0.0000            | 0.0000                                    | 0.0000      | 0.0000  | 0.0000            |
| Ethyl acetoacetate (1) + Hexan-2-one (2)  |                 |             |         |                   | Ethyl acetoacetate (1) + Nonan-2-one (2)  |             |         |                   |
| 0.0000                                    | 0.0000          | 0.0000      | 0.0000  | 0.0000            | 0.0000                                    | 0.0000      | 0.0000  | 0.0000            |
| 0.1152                                    | 0.0165          | 0.2210      | 0.1893  | 0.0667            | 0.0675                                    | 0.2838      | -0.2181 | 0.1253            |
| 0.2047                                    | 0.0263          | 0.3529      | 0.1724  | 0.1182            | 0.1077                                    | 0.4533      | -0.3722 | 0.2057            |
| 0.3106                                    | 0.0346          | 0.4643      | -0.0394 | 0.1749            | 0.1417                                    | 0.5962      | -0.2522 | 0.2795            |
| 0.4115                                    | 0.0391          | 0.5251      | -0.0286 | 0.2204            | 0.1603                                    | 0.6743      | -0.2478 | 0.3259            |
| 0.5038                                    | 0.0404          | 0.5420      | -0.0097 | 0.2503            | 0.1655                                    | 0.6961      | -0.2461 | 0.3459            |
| 0.6047                                    | 0.0386          | 0.5183      | -0.0127 | 0.2648            | 0.1582                                    | 0.6656      | -0.2525 | 0.3408            |
| 0.7006                                    | 0.0339          | 0.4548      | 0.0167  | 0.2551            | 0.1388                                    | 0.5841      | -0.2633 | 0.3076            |
| 0.8027                                    | 0.0256          | 0.3434      | -0.0065 | 0.2120            | 0.1048                                    | 0.4409      | -0.2787 | 0.2392            |
| 0.9015                                    | 0.0143          | 0.1925      | -0.5683 | 0.1301            | 0.0588                                    | 0.2472      | -0.2664 | 0.1380            |
| 1.0000                                    | 0.0000          | 0.0000      | 0.0000  | 0.0000            | 0.0000                                    | 0.0000      | 0.0000  | 0.0000            |

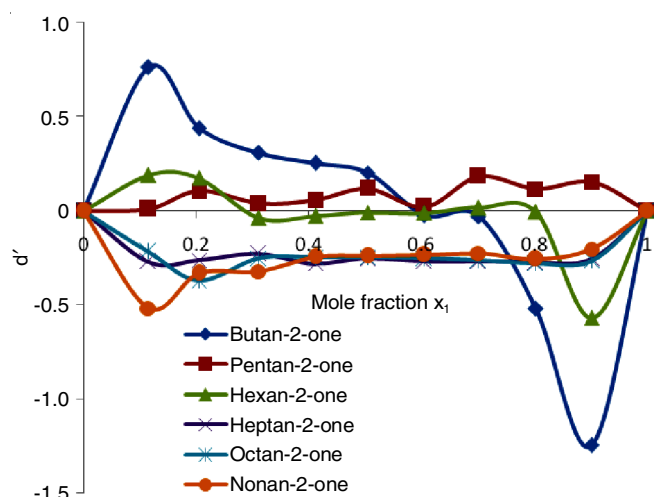


Fig. 5. Plots of Grunberg-Nissan correlation ( $d'$ ) of EAA + butan-2-one (1), + pentan-2-one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 298.15 K

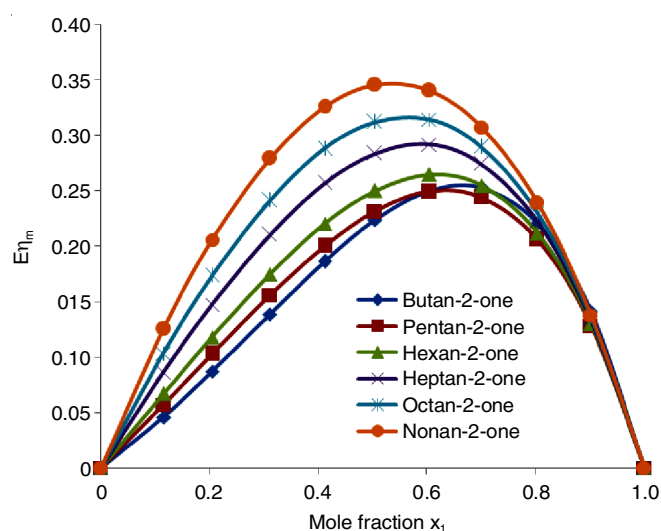


Fig. 6. Plots of Kendall and Monroe modified correlation ( $E\eta_m$ ) of EAA + butan-2-one (1), + pentan-2-one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 298.15 K

Hind and Kendall-Monroe parameters are indicative of the presence of specific interactions. The observed Grunberg-Nissan interaction parameter values in this present work revealed that

both specific and dispersive interactions are taking place, which is in accordance with the excess viscosities ( $\eta^E$ ) and excess

TABLE-8  
FITTING PARAMETERS WITH AVERAGE PERCENTAGE DEVIATION (APD) VALUES OF THE  
BINARY MIXTURES OF ETHYL ACETOACETATE AND (C<sub>4</sub> – C<sub>9</sub>) ALIPHATIC KETONES AT 298.15 K

| Binary mixtures at<br>298.15 K | Frenkel        |       | Hind        |        | Kendall-Monroe  |       | Grunberg-Nissan |       |
|--------------------------------|----------------|-------|-------------|--------|-----------------|-------|-----------------|-------|
|                                | ln $\eta_{12}$ | APD   | $\eta_{12}$ | APD    | En <sub>m</sub> | APD   | d'              | APD   |
| EAA + But-2-one                | -1.3882        | 10.38 | 11.942      | -2.001 | 1.5468          | 7.654 | 0.1402          | 8.961 |
| EAA + Pent-2-one               | -0.9103        | 9.881 | 11.442      | -0.850 | 1.5760          | 7.722 | 0.7964          | 8.399 |
| EAA + Hex-2-one                | -0.0316        | 9.116 | 11.983      | -0.759 | 1.6924          | 7.699 | -0.2866         | 9.327 |
| EAA + Hept-2-one               | 1.3845         | 8.048 | 13.059      | -0.744 | 1.9060          | 7.656 | -2.5745         | 11.03 |
| EAA + Octan-2-one              | 2.4434         | 7.414 | 14.058      | -0.555 | 2.0888          | 7.657 | -2.3643         | 10.71 |
| EAA + Nonan-2-one              | 3.5716         | 6.873 | 15.338      | -0.432 | 2.3079          | 7.658 | -0.2181         | 9.226 |

Gibbs free energy of activation for viscous flow ( $\Delta G^{\text{E}}$ ) for the solvent systems. Out of the four different equations used to correlate the experimental viscosity data, the values obtained from the Grunberg-Nissan parameter were found to be lowest. Hence, Grunberg-Nissan correlation equation is more convenient and fits better than others.

The values of Average Percentage Deviation (APD) as obtained from eqn. 12 are reported in Table-8. The APD values obtained for Hind are very small compared to Frenkel, Grunberg-Nissan and Kendall-Monroe. The values of Hind are negative while that of Frenkel, Grunberg-Nissan and Kendall-Monroe are positive. This reveals the presence of both specific and dispersive interactions in the studied solvent systems.

## Conclusion

Experimental values of viscosities of binary mixtures of ethyl acetoacetate with aliphatic (C<sub>4</sub>-C<sub>9</sub>) ketones at varying compositions were determined at 298.15 K. From this, excess functions such as  $\eta^{\text{E}}$  and  $\Delta G^{\text{E}}$  have been calculated and correlated using the Redlich-Kister polynomial. The sign and magnitude of these excess functions have been discussed in terms of dipole-dipole interactions between the component molecules and interstitial fitting between the component molecules in the systems. The excess functions were used to estimate the strength of interactions of the component molecules.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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