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## Volumetric, viscometric and optical study of molecular interactions in binary mixtures of diethyl malonate with ketones at 303.15, 308.15 and 313.15 K

MANAPRAGADA V. RATHNAM<sup>1\*</sup>, SUDHIR MOHITE<sup>1</sup>  
and MANAPRAGADA S. KUMAR<sup>2</sup>

<sup>1</sup>Physical Chemistry Research Laboratory, B. N. Bandodkar College of Science, Thane – 400 601, India and <sup>2</sup>Department of Chemistry, Zula Bhilajirao Patil College, Deopur, Dhule – 424 002, India

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**Abstract:** Density,  $\rho$ , viscosity,  $\eta$ , and refractive index,  $n_D$ , were measured for binary mixtures of diethyl malonate with ketones (acetophenone, cyclopentanone, cyclohexanone and 3-pentanone) at temperatures of 303.15, 308.15 and 313.15 K over the entire composition range. The excess volume,  $V^E$ , deviation in viscosity,  $\Delta\eta$ , excess Gibb's free energy of activation for viscous flow,  $\Delta G^E$ , and deviation in molar refraction,  $\Delta R$ , were determined from the experimental data and the computed results were fitted to the Redlich–Kister polynomial equation. The values of  $V^E$ ,  $\Delta\eta$ ,  $\Delta G^E$ , and  $\Delta R$  were plotted against the mole fraction of diethyl malonate. The observed positive and negative values of the excess parameters for all the studied binary mixtures were explained based on the intermolecular interactions present in these mixtures. Furthermore, different empirical relations were used to correlate the binary mixture viscosities and refractive indices.

**Keywords:** density; diethyl malonate; ketones; molecular interactions; excess properties.

### INTRODUCTION

Liquid–liquid mixtures due to their unusual behavior have attracted considerable attention.<sup>1</sup> The physico–chemical properties *viz.* density, viscosity, refractive index or speed of sound and the thermodynamic behavior of binary mixtures have been studied for various reasons. One of the most important of which is that these properties provide information about molecular interactions. Many engineering problems require quantitative data of the viscosity and density of liquid mixtures. Such data find extensive application in solution theory and

\* Corresponding author. E-mail: mvrathnam58@rediffmail.com  
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molecular dynamics.<sup>2</sup> Furthermore, these properties are used for the interpretation of data obtained from biochemical and kinetic studies.<sup>3</sup>

Diethyl malonate, a colorless, fragrant liquid boiling at 199 °C, is prepared by the reaction of monochloroacetic acid with methanol and carbon monoxide. It is used to synthesize barbiturates and vitamins B1 and B6 because of its typical structure consisting of two adjacent carbonyl groups. In the pharmaceutical industry, diethyl malonate is used for the synthesis of pharmaceuticals such as chloroquine. It can also be used in the pesticides, paint, spice industries, *etc.*

In general, ketoesters are highly polar and are known to self-associate through dipole–dipole interactions.<sup>4</sup> Ketones are used as solvents for insecticides, fungicides and as intermediates in the synthesis of pharmaceuticals. In particular, acetophenone is most commonly used as a flavoring agent in many cherry-flavored sweets, drinks and in chewing gum.

Thermodynamic and transport properties of binary liquid mixtures involving various types of organic solvents are replete in the literature. However, only a few studies on ketones with esters are available.<sup>5–10</sup> Pan *et al.*<sup>11</sup> studied the density and viscosity for binary mixtures containing diethyl oxalate, and dibutyl phthalate with normal alkanols at 303.15 K. Rodriguez *et al.*<sup>12</sup> reported the density and refractive index of and the speed of sound in binary mixtures (diethyl carbonate + alcohols) at several temperatures. Nayak *et al.*<sup>13</sup> studied the density, viscosity and refractive index of and the speed of sound in diethyl oxalate, diethyl phthalate and dioctyl phthalate at 298.15, 303.15 and 308.15 K. Moreover, Baragi *et al.*<sup>14</sup> studied the density, viscosity and refractive index of and speed of sound in binary mixtures of 1,4-dioxane with diethyl malonate. Likewise, thermodynamic and acoustic properties containing diethyl malonate with alcohols or hydrocarbons have been reported in the literature.<sup>15–19</sup> In continuation of our research program involving the study of excess properties<sup>20–22</sup> of binary liquid mixtures containing various types of esters, in this manuscript the experimental measurements of density,  $\rho$ , viscosity,  $\eta$ , and refractive index,  $n_D$ , for binary mixtures of diethyl malonate with ketones (acetophenone, cyclopentanone, cyclohexanone and 3-pentanone) at 303.15, 308.15 and 313.15 K and at atmospheric pressure are reported. The experimental values of  $\rho$ ,  $\eta$  and  $n_D$  were used to calculate the excess volume,  $V^E$ , the deviation in viscosity,  $\Delta\eta$ , the excess Gibb's free energy of activation for viscous flow,  $\Delta G^E$ , and the deviation in molar refraction,  $\Delta R$ . These results were used to discuss the nature of the interactions between the unlike molecules in terms of dipole–dipole interactions and dispersion forces. The refractive index data was also predicted using some of the refractive index models of mixing rules and the results are discussed in terms of the average percentage deviation (*APD*) and the standard percentage deviation,  $\sigma$ (%). The agreement between the experimental and theoretical values was found to be satisfactory. Similarly, the McAllister four-body interaction model, the

Lobe and Jouyban–Acree model were used to correlate the viscosities of the binary liquid mixtures with the mole fraction.

## EXPERIMENTAL

### Materials

Diethyl malonate, acetophenone (Sigma-Aldrich) and cyclopentanone, cyclohexanone and 3-pentanone (all Merck) with mass fraction purities greater than 99.0 % were used without further purification. The purity of the solvents was ascertained by gas liquid chromatography (GLC) and the analysis indicated a mol % purity of > 99.0 %. The experimental results of density, viscosity and refractive index of the pure liquids at 303.15 K are compared with available literature data in Table I-S of the Supplementary material.

### Methods

Binary mixtures were prepared by mass in airtight-stoppered glass bottles. The masses were recorded on a digital electronic balance (Mettler AE 240, Switzerland) to an uncertainty of  $\pm 0.0001$  g. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots *via* syringes into stoppered bottles. The uncertainty in mole fraction was thus estimated to be less than  $\pm 0.0001$ . A set of nine binary mixtures was prepared for each system, and their physical properties were measured at the respective composition of the mole fraction varying from 0.1 to 0.9 in steps of 0.1.

The densities of the pure liquids and their binary mixtures were determined with a portable density meter (DMA 35 Anton Paar). The instrument was calibrated frequently before the start of the actual experiments using deionized water and dry air according to established standard procedures. The instrument has a temperature sensor that measures the sample temperature right at the measuring cell. The densities of all the binary mixtures were measured after achieving thermal equilibrium with successive increments of 5 K for the temperature range from 303.15 to 313.15 K. All measurements for each sample were made in triplicate; the average values are reported and considered for further analysis. The reproducibility of the density measurements was  $\pm 0.0005$  g cm<sup>-3</sup> and the experimental uncertainty in the density measurements was approximately  $\pm 3 \times 10^{-4}$ .

The viscosities of the pure liquids and their mixtures were determined at atmospheric pressure and at temperatures 303.15, 308.15 and 313.15 K using an Ubbelohde viscometer. The viscometer bulb had a capacity of about 15 ml and the capillary tube had a length of about 90 mm with an internal diameter of 0.5 mm. The thoroughly cleaned and perfectly dried viscometer was filled with the sample liquid by fitting the viscometer to about 30° from the vertical and its limbs were closed with Teflon® caps to avoid the evaporation. The viscometer was kept in a transparent-walled bath with a thermal stability of  $\pm 0.01$  K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of  $\pm 0.01$  s was used for flow time measurements. At least three repetitions of each mixture reproducible to  $\pm 0.05$  s were obtained, and the results were averaged. The viscosity was calculated from measured efflux time,  $t$ , using the following relation:

$$\eta = \rho (At - B/t) \quad (1)$$

where  $\rho$  is the density and  $A$  and  $B$  are characteristic constants of the viscometer, which were determined by taking water and benzene as calibration liquids. The uncertainty in the thus estimated viscosity was found to be  $\pm 0.008$  mPa s.

Refractive indices were measured using a refractometer (RM40, Mettler Toledo, Switzerland) with an uncertainty of  $\pm 0.0001$ . The instrument had a built-in solid state thermostat

temperature range (5 to 100 °C) with an uncertainty of  $\pm 0.1$  °C. The instrument calibration was realized with doubly distilled water. The average of three measurements was taken for each sample.

## RESULTS AND DISCUSSION

### *Experimental data and excess or deviation values*

The densities,  $\rho$ , viscosities,  $\eta$ , and refractive indices  $n_D$  of the mixtures at 303.15, 308.15 and 313.15 K are listed as a function of mole fraction in Table II-S of the Supplementary material.

The density values were used to calculate the excess molar volumes,  $V^E$ , using the following relation:

$$V^E = (x_1 M_1 + x_2 M_2) / \rho - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \quad (2)$$

where  $\rho$  is the density of the mixture and  $x_1$ ,  $M_1$  and  $\rho_1$ , and  $x_2$ ,  $M_2$  and  $\rho_2$ , are the mole fraction, molar mass, and density of pure components 1 and 2, respectively. The calculated excess molar volumes are included in Table II-S and graphically represented in Fig 1.

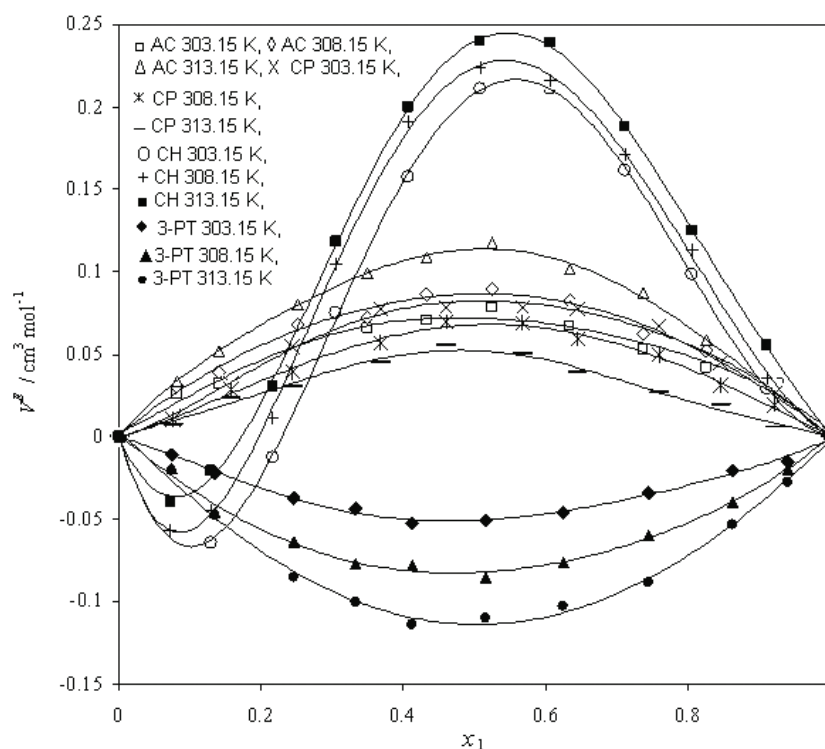


Fig. 1. Excess volume,  $V^E$ , as a function of diethyl malonate mole fraction,  $x_1$  + acetophenone (AC); + cyclopentanone (CP); + cyclohexanone (CH); + 3-pentanone (3-PT).

The deviations in the viscosity,  $\Delta\eta$ , were calculated using the relation:

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (3)$$

where  $\eta$  is the absolute viscosity of the mixture, and  $\eta_1$  and  $\eta_2$  are the viscosities of the pure components 1 and 2, respectively. The  $\Delta\eta$  data are graphically represented in Fig. 2.

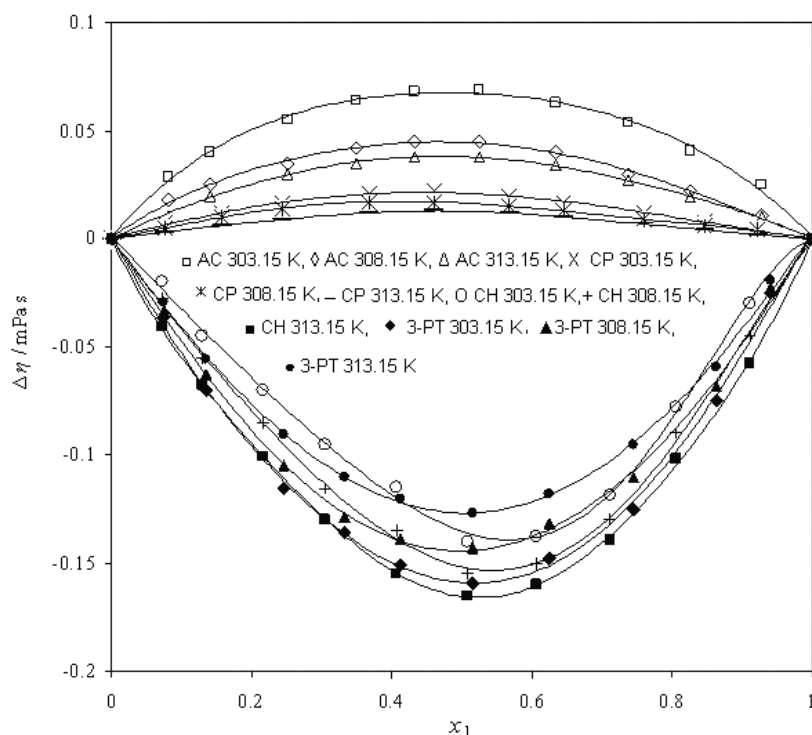


Fig. 2. Deviation in viscosity,  $\Delta\eta$ , as a function of diethyl malonate mole fraction,  $x_1$  + acetophenone (AC); + cyclopentanone (CP); + cyclohexanone (CH); + 3-pentanone (3-PT).

The excess Gibb's energy of activation,  $\Delta G^E$ , of viscous flow was obtained using the following relation:

$$\Delta G^E = RT(\ln(\eta V) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2)) \quad (4)$$

where  $V$  is the molar volume of the mixture and  $V_1$  and  $V_2$  are the molar volumes of the pure components 1 and 2, respectively. The  $\Delta G^E$  data are graphically represented in Fig. 3.

The refractive index values,  $n$ , were used to calculate the Lorentz-Lorentz molar refraction,<sup>23</sup> and deviations in the molar refraction were calculated as:

$$\Delta R = R_m - (x_1 R_1 + x_2 R_2) \quad (5)$$

where  $R_1$  and  $R_2$  are the molar refractivities of pure components 1 and 2, respectively, and  $R_m$  is the molar refractivity of the mixtures calculated by using the relation:

$$R_m = ((n^2 - 1) / (n^2 + 2)) / ((x_1 M_1 + x_2 M_2) / \rho) \quad (6)$$

The so-obtained  $\Delta R$  data are graphically represented in Fig. 4.

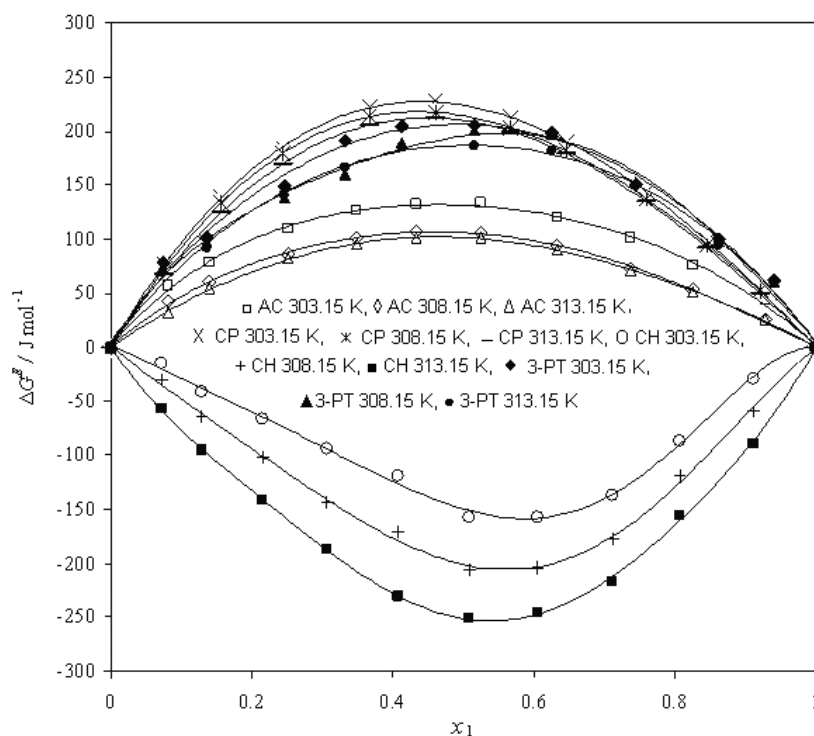


Fig. 3. Excess Gibbs Energy,  $\Delta G^E$ , as a function of diethyl malonate mole fraction,  $x_1$  + acetophenone (AC); + cyclopentanone (CP); + cyclohexanone (CH); + 3-pentanone (3-PT).

All of the quantities ( $V^E$ ,  $\Delta\eta$ ,  $\Delta G^E$  and  $\Delta R$ ) were fitted to the Redlich–Kister<sup>24</sup> polynomial equation by the method of least squares to derive the binary coefficients:

$$\Delta y = x_1(1 - x_1) \sum_{i=0}^n A_i (2x_1 - 1)^i \quad (7)$$

The variation in standard deviation ( $\sigma$ ) was calculated using the relation:

$$\sigma(y) = (\sum (y_{\text{obs}} - y_{\text{cal}})^2 / (n - m))^{1/2} \quad (8)$$

where  $n$  represents the number of data points and  $m$  is the number of coefficients. The calculated values of coefficients along with the standard deviations ( $\sigma$ ) are given in Table I.

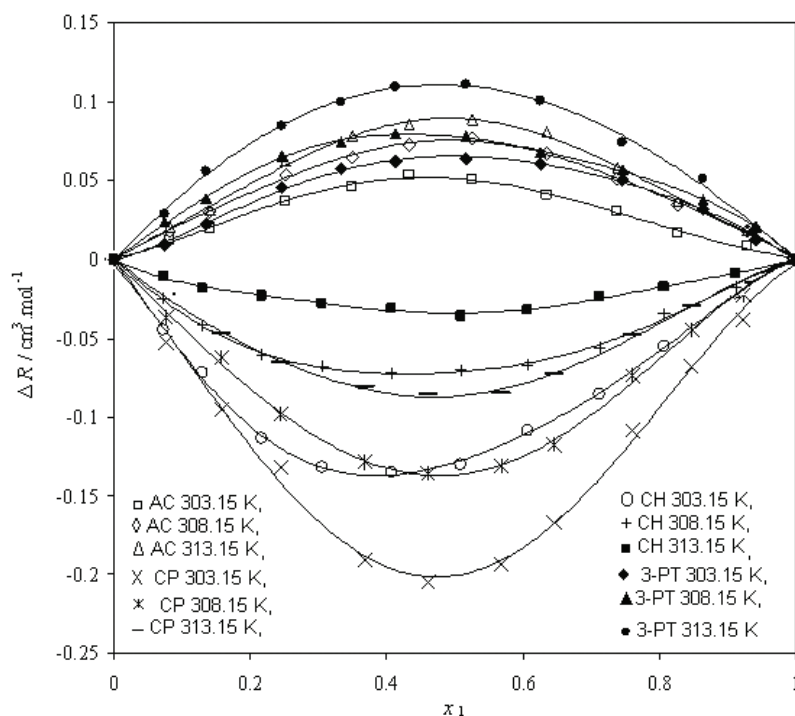


Fig. 4. Deviation in molar refraction,  $\Delta R$ , as a function of diethyl malonate mole fraction,  $x_1$  + acetophenone (AC); + cyclopentanone (CP); + cyclohexanone (CH); + 3-pentanone (3-PT).

TABLE I. Derived parameters of Eq. (7) for various functions and standard deviation ( $\sigma$ ) of the binary mixtures at 303.15, 308.15 and 313.15 K

| Function                                | $T/K$  | $A_0$    | $A_1$    | $A_2$    | $A_3$    | $\sigma$ |
|---|--------|----------|----------|----------|----------|----------|
| Diethyl malonate (1) + acetophenone (2) |        |          |          |          |          |          |
| $n^E$                                   | 303.15 | 0.2699   | -0.0155  | 0.0981   | -0.0084  | 0.002    |
|   | 308.15 | 0.3453   | 0.0153   | 0.0076   | -0.0333  | 0.004    |
|   | 313.15 | 0.4504   | 0.0366   | -0.0692  | -0.1189  | 0.003    |
| $\Delta\eta$                            | 303.15 | 0.2699   | -0.0155  | 0.0981   | -0.0084  | 0.002    |
|   | 308.15 | 0.1775   | -0.0229  | 0.0039   | -0.0345  | 0.001    |
|   | 313.15 | 0.1517   | -0.0227  | -0.0079  | 0.0143   | 0.001    |
| $\Delta R$                              | 303.15 | 0.2036   | -0.0618  | -0.1182  | 0.0500   | 0.002    |
|   | 308.15 | 0.2979   | -0.0175  | -0.0898  | 0.0193   | 0.002    |
|   | 313.15 | 0.3518   | -0.0260  | -0.1566  | 0.0275   | 0.003    |
| $\Delta G^E$                            | 303.15 | 524.3250 | -57.1088 | 163.6531 | -27.5843 | 3.539    |
|   | 308.15 | 422.6787 | -66.2303 | 18.3785  | -66.5172 | 5.551    |
|   | 313.15 | 404.1643 | -68.1976 | -8.5612  | 23.7000  | 1.466    |

TABLE I. Continued

| Function                                  | $T / K$ | $A_0$     | $A_1$     | $A_2$    | $A_3$     | $\sigma$ |
|---|---------|-----------|-----------|----------|-----------|----------|
| Diethyl malonate (1) + cyclopentanone (2) |         |           |           |          |           |          |
| $V^E$                                     | 303.15  | 0.3304    | 0.0120    | -0.0616  | 0.1423    | 0.003    |
|   | 308.15  | 0.2703    | 0.0290    | -0.1013  | 0.0249    | 0.003    |
|   | 313.15  | 0.2052    | -0.0338   | -0.1370  | 0.0204    | 0.003    |
| $\Delta\eta$                              | 303.15  | 0.0846    | -0.0238   | -0.0191  | 0.0022    | 0.001    |
|   | 308.15  | 0.0656    | -0.0332   | -0.0081  | 0.0290    | 0.000    |
|   | 313.15  | 0.0505    | -0.0125   | -0.0250  | 0.0051    | 0.000    |
| $\Delta R$                                | 303.15  | -0.8002   | 0.1332    | 0.3718   | -0.0028   | 0.007    |
|   | 308.15  | -0.5458   | 0.0791    | 0.2558   | 0.0616    | 0.004    |
|   | 313.15  | -0.3462   | 0.0611    | 0.1225   | 0.0404    | 0.002    |
| $\Delta G^E$                              | 303.15  | 893.7855  | -216.1805 | 13.3465  | -1.8419   | 1.130    |
|   | 308.15  | 856.6069  | -228.7443 | 24.9172  | 51.6539   | 0.381    |
|   | 313.15  | 836.9972  | -182.8202 | -19.9603 | 16.6195   | 0.401    |
| Diethyl malonate (1) + cyclohexanone (2)  |         |           |           |          |           |          |
| $V^E$                                     | 303.15  | 0.8241    | 0.5942    | -1.5870  | 0.1723    | 0.003    |
|   | 308.15  | 0.8975    | 0.3965    | -1.4937  | 0.4915    | 0.005    |
|   | 313.15  | 0.9476    | 0.4495    | -1.2831  | 0.3316    | 0.004    |
| $\Delta\eta$                              | 303.15  | -0.5462   | -0.2207   | 0.2528   | 0.3333    | 0.003    |
|   | 308.15  | -0.6070   | -0.1422   | 0.1618   | 0.1496    | 0.003    |
|   | 313.15  | -0.6537   | -0.0865   | 0.0319   | 0.0593    | 0.003    |
| $\Delta R$                                | 303.15  | -0.5224   | 0.2712    | 0.0495   | -0.0556   | 0.003    |
|   | 308.15  | -0.2905   | 0.0613    | -0.0117  | 0.0873    | 0.002    |
|   | 313.15  | -0.1338   | 0.0027    | 0.0172   | 0.0522    | 0.002    |
| $\Delta G^E$                              | 303.15  | -606.8685 | -369.8802 | 375.6739 | 527.3885  | 5.562    |
|   | 308.15  | -804.4342 | -295.0760 | 288.3852 | 300.8933  | 5.448    |
|   | 313.15  | -990.5262 | -219.4471 | 108.3232 | 146.5062  | 5.365    |
| Diethyl malonate (1) + 3-pentanone (2)    |         |           |           |          |           |          |
| $V^E$                                     | 303.15  | -0.2039   | 0.0412    | 0.0346   | -0.0952   | 0.002    |
|   | 308.15  | -0.3303   | 0.0391    | -0.0235  | -0.0562   | 0.004    |
|   | 313.15  | -0.4549   | 0.05565   | 0.0368   | -0.2077   | 0.003    |
| $\Delta\eta$                              | 303.15  | -0.6370   | -0.0554   | 0.0660   | 0.0845    | 0.004    |
|   | 308.15  | -0.5786   | 0.0052    | 0.0676   | -0.0248   | 0.004    |
|   | 313.15  | -0.5071   | -0.0271   | 0.0676   | 0.0578    | 0.003    |
| $\Delta R$                                | 303.15  | 0.2608    | -0.0043   | -0.0575  | 0.0992    | 0.002    |
|   | 308.15  | 0.3112    | -0.0878   | 0.0389   | 0.1473    | 0.001    |
|   | 313.15  | 0.4423    | -0.0568   | -0.0319  | 0.0299    | 0.003    |
| $\Delta G^E$                              | 303.15  | 821.9431  | -18.5135  | 124.3100 | -9.8292   | 10.572   |
|   | 308.15  | 777.7993  | 165.4446  | 144.2818 | -309.9339 | 9.692    |
|   | 313.15  | 746.4863  | 34.3000   | 166.5115 | -37.4047  | 7.395    |

The excess molar volume curves (Fig. 1) are not symmetric. The  $V^E$  values for the systems diethyl malonate + acetophenone and + cyclopentanone are completely positive, the maximum values of isotherms fall around the mole fraction  $x_1 = 0.5$ , while for diethyl malonate + 3-pentanone, they are completely negative over the entire composition range, having minima at  $x_1 = 0.5$ . However, for the



system diethyl malonate + cyclohexanone, the  $V^E$  values are negative in the lower composition of ester ( $x_1 = 0.2$ ) at 303.15, 308.15 and 313.15 K, and the  $V^E$  values become positive as the composition of ester increases. The positive values of  $V^E$  suggest the dominance of dispersion forces while the negative values of  $V^E$  suggest specific interactions between the unlike molecules of the binary liquid systems.<sup>25,26</sup> In the present study, the unusual behavior as observed for diethyl malonate + cyclohexanone indicates that the strengths of the specific or dispersion forces are not the only factor influencing the excess volume of the liquid mixtures but the molecular size and shape of the component also play a dominant role in deciding the deviation from ideality. Moreover, it was observed in many binary systems that there is no simple correlation between strength of the interactions and the observed properties. Accordingly, Rastogi *et al.*<sup>27</sup> suggested that the observed excess property is a combination of an interaction and non-interaction part, the non interaction part being the size effect, *i.e.*,

$$X^E_{(\text{observed})} = X^E_{(\text{interaction})} + X^E_{(\text{size effect})}$$

where  $X^E$  refers to the excess or deviation in the property.

A perusal of (Fig. 2) reveals that the  $\Delta\eta$  values for the binary mixtures of diethyl malonate with acetophenone and with cyclopentanone are completely positive, while for diethyl malonate + cyclohexanone and + 3-pentanone, the  $\Delta\eta$  values are completely negative over the entire range of composition at all the studied temperatures. The positive  $\Delta\eta$  values decrease with increasing temperature. The negative  $\Delta\eta$  values become more negative as the temperature increases for diethyl malonate + cyclohexanone, whereas less negative for diethyl malonate + 3-pentanone. The positive  $\Delta\eta$  values are indicative of specific interactions,<sup>28-30</sup> while the negative  $\Delta\eta$  values indicate that dispersion forces are dominant; furthermore, the existence of dispersion forces indicates that the component molecules have different molecular sizes and shapes.<sup>31</sup>

The values of  $\Delta G^E$  (Fig. 3) for the binary mixtures of diethyl malonate with acetophenone, cyclopentanone and 3-pentanone are completely positive over the entire composition; while for the mixtures of with cyclohexanone, the values are completely negative all the studied temperatures. The positive  $\Delta G^E$  values decrease with increasing temperature, whereas the negative  $\Delta G^E$  values become more negative.

The dependences of the molar refraction,  $\Delta R$ , on the mole fraction of diethyl malonate at 303.15, 308.15 and 313.15 K are presented in Fig. 4. It is observed that for the mixtures with acetophenone and 3-pentanone,  $\Delta R$  is completely positive, while for the mixtures with cyclopentanone and cyclohexanone, the  $\Delta R$  values are completely negative over the entire range of composition. The positive  $\Delta R$  values increase with increasing temperature, whereas the negative  $\Delta R$  values

become less negative. The plots are of parabolic shape and are characterized by the presence of well-defined minima/maxima.

#### *Correlating models for mixture viscosities*

The experimental viscosities of the binary mixtures of diethyl malonate with acetophenone, cyclopentanone, cyclohexanone and 3-pentanone at 303.15, 308.15 and 313.15 K were fitted to the two parameter Lobe,<sup>32</sup> the three parameter McAllister four-body<sup>33</sup> and the three parameter Jouyban–Acree<sup>34,35</sup> models.

The Lobe Equation involves the volume fraction of components  $\Phi_1$  and  $\Phi_2$  and was tested by fitting with two parameter,  $\alpha_{12}$  and  $\alpha_{21}$ , to the kinematic viscosity–mole fraction ( $\nu, x_1$ ) data pairs and is given by:

$$\nu = \Phi_1 \nu_1 \exp(\Phi_2 \alpha_{12} \ln(\nu_2/\nu_1)) + \Phi_2 \nu_2 \exp(\Phi_1 \alpha_{21} \ln(\nu_2/\nu_1)) \quad (9)$$

The McAllister (four-body) Model applied to correlate kinematic viscosities of binary liquid mixtures is given by:

$$\begin{aligned} \ln \nu = & x_1 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \\ & - \ln [x_1 + (x_2 M_2/M_1)] + 4x_1^3 x_2 \ln \{[3 + (M_2/M_1)]/4\} + 6x_1^2 x_2^2 \times \\ & \times \ln \{[1 + (M_2/M_1)]/2\} + 4x_1 x_2^3 \ln \{[1 + (3M_2/M_1)]/4\} + x_2^4 \ln (M_2/M_1) \end{aligned} \quad (10)$$

where  $\nu$ ,  $\nu_1$  and  $\nu_2$  are the kinematic viscosities of the binary mixtures and the pure components 1 and 2, respectively.  $\nu_{1112}$ ,  $\nu_{1122}$  and  $\nu_{2221}$  are model parameters, which are obtained by non-linear regression.

The Jouyban–Acree Model is based on a theoretical consideration of two-body and three-body interactions between the various molecules in solution. The model could be used in practice for correlating the experimental viscosity data of different binary mixtures at various temperatures as:

$$\begin{aligned} \ln \eta = & x_1 \ln \eta_1 + x_2 \ln \eta_2 + A_0(x_1 x_2/T) + A_1(x_1 x_2(x_1 - x_2)/T) + \\ & + A_2(x_1 x_2(x_1 - x_2)^2/T) \end{aligned} \quad (11)$$

where  $A_0$ ,  $A_1$  and  $A_2$  are interaction parameters.  $\eta_1$  and  $\eta_2$  are the viscosity of the pure components at temperature  $T$ . The predictive ability of Eqs. (9)–(11) was tested by calculating the standard percentage deviation  $\sigma$  (%) as:

$$\sigma(\%) = (1/n - k \sum (100(Y_{\text{exp}} - Y_{\text{cal}})/Y_{\text{exp}})^2)^{1/2} \quad (12)$$

and the average percentage deviation ( $APD$ ) using the relation:

$$APD = 100 \sum_{i=1}^n (|Y_{\text{exp}} - Y_{\text{cal}}|) / n \quad (13)$$

between the experimental and the calculated values;  $n$  represents the number of data points in each set and  $k$  the number of numerical coefficients in the equations,  $Y$  indicates the respective correlating property. The deviation values of Eqs. (12) and (13) obtained using the experimental viscosity data are given in Table II.

TABLE II. Adjustable parameters, standard percentage deviation,  $\sigma$ , and average percentage deviation ( $APD$ ) of the correlations for the viscosities

| $T / K$ | Lobe                                     |               |                   | McAllister four-body model |            |            |                   |                   | Jouyban-Acree model |           |          |                   |
|---------|--|---------------|-------------------|----------------------------|------------|------------|-------------------|-------------------|---------------------|-----------|----------|-------------------|
|         | $\alpha_{12}$                            | $\alpha_{21}$ | $\sigma / \% APD$ | $v_{1112}$                 | $v_{1122}$ | $v_{2221}$ | $\sigma / \% APD$ | $\sigma / \% APD$ | $A_0$               | $A_1$     | $A_2$    | $\sigma / \% APD$ |
|         | Diethyl malonate (1) + acetophenone (2)  |               |                   |                            |            |            |                   |                   |                     |           |          |                   |
| 303.15  | 2.5338                                   | -3.6895       | 0.23              | 1.7012                     | 1.6285     | 1.7565     | 0.13              | 0.11              | 51.8696             | -7.0372   | 19.7008  | 0.36              |
| 308.15  | 0.1615                                   | -1.0233       | 0.09              | 1.5106                     | 1.4928     | 1.5635     | 0.10              | 0.09              | 39.0955             | -9.6821   | 2.4985   | 0.16              |
| 313.15  | 2.5387                                   | -3.2133       | 0.06              | 1.4074                     | 1.3989     | 1.4538     | 0.05              | 0.04              | 36.4069             | -6.0723   | -1.1598  | 0.12              |
|         | Diethyl malonate (1) + cyclopentanone(2) |               |                   |                            |            |            |                   |                   |                     |           |          |                   |
| 303.15  | 2.2762                                   | -1.8436       | 0.08              | 1.5327                     | 1.4164     | 1.4966     | 0.05              | 0.05              | 63.6068             | -18.0848  | 0.2274   | 0.29              |
| 308.15  | 2.3538                                   | -1.8730       | 0.08              | 1.4022                     | 1.2984     | 1.3793     | 0.04              | 0.03              | 58.4043             | -17.1637  | 1.7784   | 0.28              |
| 313.15  | 2.0911                                   | -1.6750       | 0.10              | 1.3042                     | 1.2148     | 1.2788     | 0.02              | 0.03              | 55.5530             | -13.1099  | -3.8643  | 0.23              |
|         | Diethyl malonate (1) + cyclohexanone (2) |               |                   |                            |            |            |                   |                   |                     |           |          |                   |
| 303.15  | -15.8419                                 | 5.5224        | 0.98              | 1.6873                     | 1.2947     | 2.4875     | 0.71              | 0.55              | -99.5588            | -114.2321 | 196.5356 | 3.71              |
| 308.15  | -6.9947                                  | 2.4203        | 0.19              | 1.4321                     | 1.4048     | 1.8077     | 0.18              | 0.13              | -117.109            | -18.5453  | 26.3678  | 0.57              |
| 313.15  | -6.8777                                  | 2.1691        | 0.27              | 1.3153                     | 1.2982     | 1.6627     | 0.31              | 0.24              | -133.787            | -16.9713  | 18.8131  | 0.61              |
|         | Diethyl malonate (1) + 3-pentanone (2)   |               |                   |                            |            |            |                   |                   |                     |           |          |                   |
| 303.15  | 1.0578                                   | -0.8175       | 0.39              | 1.3228                     | 0.9806     | 0.8749     | 0.39              | 0.38              | 79.6830             | -0.3868   | 14.5896  | 0.49              |
| 308.15  | 0.9304                                   | -0.6452       | 0.45              | 1.2180                     | 0.8947     | 0.8004     | 0.42              | 0.39              | 73.9628             | 8.8340    | 18.0103  | 0.53              |
| 313.15  | 1.0170                                   | -0.7425       | 0.35              | 1.1437                     | 0.8493     | 0.7771     | 0.27              | 0.25              | 70.5074             | 4.8170    | 19.7092  | 0.38              |

A close examination of these values reveals that the magnitude of these values remained almost same, with the exception for the Jouyban–Acree Model, for which the obtained *APD* values were much lower in comparison to the standard percentage deviation  $\sigma$  (%) values. While for the mixtures of diethyl malonate + 3-pentanone, the same trend was observed for all three studied models. Furthermore, it was observed that the McAllister four-body Model correlates the mixture viscosities excellently when compared to the Lobe and Jouyban–Acree Models.

#### *Correlating models for refractive index*

The experimental refractive index and density data of the studied binary mixtures were correlated using empirical/semi-empirical relations and models as reported earlier.<sup>36</sup> The experimental refractive index data were then compared with the corresponding Lorentz–Lorentz,<sup>37,38</sup> Weiner,<sup>37,38</sup> Heller,<sup>37,38</sup> Eykman,<sup>39</sup> Newton,<sup>40</sup> Eyring–John<sup>41</sup> and Dale–Gladstone<sup>42</sup> relations.

The values of standard percentage deviation,  $\sigma$  (%), and average percentage deviation (*APD*) as obtained from Eqs. (12) and (13) are reported in Table III. Comparison of these values revealed that  $\sigma$  values were small in magnitude as compared to the values of *APD*. For diethyl malonate + 3-pentanone, the maximum *APD* (0.164) was obtained using the Eykman Relation while the minimum *APD* (0.024) was obtained using the Weiner relation. Whereas, for diethyl malonate + cyclopentanone system, the *APD* values are quite higher (maximum 0.274 by the Eykman and minimum 0.033 by the Weiner Relation) as compared to the

TABLE III. Average percentage deviation (*APD*) and standard percentage deviation,  $\sigma$ , in the refractive index from different mixing relations

| <i>T</i> / K                              | Lorentz–Lorentz |              | Eykman     |              | Weiner     |              | Heller     |              | Dale–Gladstone |              | Newton     |              | Eyring–John |              |
|---|-----------------|--------------|------------|--------------|------------|--------------|------------|--------------|----------------|--------------|------------|--------------|-------------|--------------|
|   | <i>APD</i>      | $\sigma$ / % | <i>APD</i> | $\sigma$ / % | <i>APD</i> | $\sigma$ / % | <i>APD</i> | $\sigma$ / % | <i>APD</i>     | $\sigma$ / % | <i>APD</i> | $\sigma$ / % | <i>APD</i>  | $\sigma$ / % |
| Diethyl malonate (1) + acetophenone (2)   |                 |              |            |              |            |              |            |              |                |              |            |              |             |              |
| 303.15                                    | 0.013           | 0.011        | 0.049      | 0.022        | 0.010      | 0.010        | 0.040      | 0.020        | 0.065          | 0.026        | 0.151      | 0.039        | 0.023       | 0.015        |
| 308.15                                    | 0.024           | 0.015        | 0.023      | 0.015        | 0.003      | 0.006        | 0.044      | 0.021        | 0.044          | 0.021        | 0.129      | 0.036        | 0.005       | 0.007        |
| 313.15                                    | 0.026           | 0.016        | 0.017      | 0.013        | 0.005      | 0.007        | 0.048      | 0.023        | 0.040          | 0.020        | 0.124      | 0.035        | 0.009       | 0.009        |
| Diethyl malonate (1) + cyclopentanone (2) |                 |              |            |              |            |              |            |              |                |              |            |              |             |              |
| 303.15                                    | 0.114           | 0.034        | 0.274      | 0.052        | 0.073      | 0.027        | 0.216      | 0.047        | 0.219          | 0.047        | 0.223      | 0.048        | 0.218       | 0.047        |
| 308.15                                    | 0.079           | 0.028        | 0.189      | 0.044        | 0.056      | 0.022        | 0.149      | 0.039        | 0.152          | 0.039        | 0.155      | 0.040        | 0.150       | 0.039        |
| 313.15                                    | 0.052           | 0.023        | 0.126      | 0.035        | 0.033      | 0.018        | 0.098      | 0.031        | 0.101          | 0.032        | 0.104      | 0.031        | 0.099       | 0.032        |
| Diethyl malonate (1) + cyclohexanone (2)  |                 |              |            |              |            |              |            |              |                |              |            |              |             |              |
| 303.15                                    | 0.087           | 0.029        | 0.214      | 0.046        | 0.057      | 0.024        | 0.166      | 0.041        | 0.174          | 0.042        | 0.182      | 0.043        | 0.170       | 0.041        |
| 308.15                                    | 0.057           | 0.024        | 0.143      | 0.038        | 0.038      | 0.019        | 0.109      | 0.033        | 0.117          | 0.034        | 0.125      | 0.035        | 0.113       | 0.034        |
| 313.15                                    | 0.047           | 0.022        | 0.119      | 0.034        | 0.032      | 0.018        | 0.090      | 0.030        | 0.097          | 0.031        | 0.105      | 0.032        | 0.093       | 0.031        |
| Diethyl malonate (1) + 3-pentanone (2)    |                 |              |            |              |            |              |            |              |                |              |            |              |             |              |
| 303.15                                    | 0.038           | 0.020        | 0.088      | 0.030        | 0.024      | 0.015        | 0.071      | 0.027        | 0.069          | 0.026        | 0.066      | 0.026        | 0.070       | 0.027        |
| 308.15                                    | 0.053           | 0.023        | 0.121      | 0.035        | 0.033      | 0.018        | 0.098      | 0.031        | 0.095          | 0.031        | 0.092      | 0.030        | 0.097       | 0.031        |
| 313.15                                    | 0.071           | 0.027        | 0.164      | 0.040        | 0.044      | 0.021        | 0.131      | 0.036        | 0.129          | 0.036        | 0.126      | 0.035        | 0.130       | 0.036        |

diethyl malonate + cyclohexanone system. For diethyl malonate + acetophenone, all the mixing rules, except the Newton Relation, exhibited low  $APD$  values with a maximum (0.065) by the Dale–Gladstone and the minimum (0.003) by Weiner Relation. Furthermore, it was observed that temperature has an effect on  $\sigma$  values. For the binary mixtures of diethyl malonate + cyclopentanone and diethyl malonate + cyclohexanone, the values were found to decrease with increasing temperature, while for the binary mixtures of diethyl malonate + 3-pentanone, the values increased with increasing temperature. However, for the binary mixtures of diethyl malonate + acetophenone, the values of  $\sigma$  and  $APD$  did not exhibit any systematic variation with temperature. Based on the present analysis, it could be concluded that all the studied mixing rules predicted the experimental refractive index data satisfactorily.

#### CONCLUSIONS

The density, viscosity and refractive index measurements for binary mixture of diethyl malonate + acetophenone, + cyclopentanone, + cyclohexanone and + 3-pentanone at 303.15, 308.15 and 313.15 K over the entire composition range were determined. From the experimental data, the excess volume,  $V^E$ , deviations in viscosity,  $\Delta\eta$ , molar refraction,  $\Delta R$ , and excess Gibb's Free Energy of activation of flow,  $\Delta G^E$ , were obtained. The reported excess properties showed both positive and negative deviations. These excess properties were correlated by the Redlich–Kister polynomial equation to derive the coefficients and standard deviations. The viscosity results were also analyzed using the empirical relations proposed by Lobe, McAllister and Jouyban–Acree. Furthermore, the refractive indices of the binary mixtures were correlated using various empirical/semi-empirical relations and models.

#### SUPPLEMENTARY MATERIAL

The comparison of experimental results and literature data (Tables I-S and II-S) are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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## ИЗВОД

## СТУДИЈА ВОЛУМЕТРИЈСКИХ, ВИСКОЗИМЕТРИЈСКИХ И ОПТИЧКИХ СВОЈСТАВА И МОЛЕКУЛСКИХ ИНТЕРАКЦИЈА У БИНАРНОЈ СМЕШИ ДИЕТИЛМАЛОНАТА И КЕТОНА НА 303,15, 308,15 И 313,15 К

MANAPRAGADA V. RATHNAM<sup>1</sup>, SUDHIR MOHITE<sup>1</sup> и MANAPRAGADA S. KUMAR<sup>2</sup><sup>1</sup>Physical Chemistry Research Laboratory, B. N. Bandodkar College of Science, Thane – 400 601, India u<sup>2</sup>Department of Chemistry, Zulai Bhilajirao Patil College, Deopur, Dhule – 424 002, India

Извршена су мерења густине,  $\rho$ , вискозности,  $\eta$ , и индекса рефракције,  $n_D$ , бинарних смеша диетилмалоната са кетонима (ацетофенон, циклопентанон, циклохексанон и 3-пентанон) на температурама 303,15, 308,15 и 313,15 К и у целом концентрационом опсегу. На основу експерименталних података, одређене су допунска запремина,  $V^E$ , промена вискозности при мешању,  $\Delta\eta$ , допунска Гибсова слободна енергија,  $\Delta G^E$ , и промена моларне рефракције при мешању,  $\Delta R$ . Добијене вредности су корелисане Редлих–Кистер-овим полиномом. Вредности  $V^E$ ,  $\Delta\eta$ ,  $\Delta G^E$  и  $\Delta R$  су приказане графички у зависности од молског удела диетилмалоната. Позитивне и негативне вредности допунских својстава за све испитиване бинарне смеше су објашњене на основу међумолекулских интеракција присутних у овим смешама. Поред тога, извршено је корелисање вискозности и индекса рефракције бинарних смеша преко различитих емпиријских корелација.

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