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# Interaction Study on Diethyl Maleate + Ketone Binary Mixtures: Application of PFP Theory to Excess Volumes

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## Abstract

Density ($\rho$), viscosity ($\eta$), and refractive index ($n_D$) for binary mixtures of diethyl maleate with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone have been measured at (303.15, 308.15 and 313.15) K over the entire range of composition of ester. From the experimental data, excess volumes ($V^E$), deviation in viscosity ($\Delta\eta$), excess Gibb's free energy of activation of viscous flow ($\Delta G^E$) and deviation in molar refraction ($\Delta R$) were calculated. The experimental viscosity data were correlated with Grunberg-Nissan, Eyring-Vanlaar, Heric-Brewer, and McAllister four body equations. The predictive ability of some of the available mixing rules of refractive index has been tested. Further Prigogine-Flory-Patterson (PFP) theory has been applied to the experimental excess volume data at equimolar concentration.

*Keywords: Density, Viscosity, Excess volume, Diethyl maleate, Ketones*

## 1. Introduction

The study of physico-chemical properties of multi components mixtures is requisite for many chemical process industries. An investigation in the possible change in physical property of a liquid mixture and its extent of deviation from ideality has been found to be an excellent qualitative way to elicit information about molecular structure, and intermolecular forces in liquid mixtures. Diethyl maleate is a colorless oily transparent liquid. It is mainly used to produce organic phosphorous pesticides called malathion, that is widely used in agriculture, residential land and scalping, public recreation areas, and in public health pest control programs such as mosquito eradication. Diethyl maleate also plays an important role in production of pharmaceutical and fragrance intermediates.

Survey of literature reveals that, to the best of our knowledge there are no reports on physico-chemical properties for the binary mixtures of diethyl maleate. This has mainly created us an interest to choose the diethyl maleate with an objective to investigate the molecular interactions of diethyl maleate + ketone binary mixtures. Suheyla and Tugba (1) have determined liquid-liquid equilibrium (LLE) of water-carboxylic acid-diethyl maleate ternary liquid systems at 298.15 K. In continuation of our earlier works (2-5), we report in this paper density ($\rho$), viscosity ($\eta$), and refractive index ($n_D$) for the binary mixtures of diethyl maleate + acetophenone, + cyclopentanone, + cyclohexanone, and + 3-pentanone at (303.15, 308.15 and 313.15) K over the entire composition range of ester. From the experimental data excess volumes ($V^E$), deviation in viscosity ($\Delta\eta$), excess Gibb's free energy of activation of viscous flow ($\Delta G^E$) and deviation in molar refraction ($\Delta R$) have been calculated. These parameters were fitted to the Redlich-Kister polynomial (6) equation by multi parametric nonlinear regression analysis to derive the binary coefficients and to estimate the standard errors ($\sigma$). The viscosities of the studied binary mixtures were correlated using empirical or semi-empirical equations. The refractive index data was also predicted using some of the refractive index models of mixing rules and the results were analyzed in terms of the average percentage deviation (APD). Lastly the applicability of Prigogine-Flory-Pattterson (PFP) theory to the excess volume data at equimolar concentration has been tested.

## 2. Experimental

Diethyl maleate (Alfa-Aesar) > 98 %, acetophenone (Sigma-Aldrich) > 99 %, cyclopentanone, cyclohexanone, and 3-pentanone all (Merck-India) of purity > 99 % were used without further purification in the present study. However before use all the chemicals were stored over 0.4 nm molecular sieves for about 72 hours to reduce water content if any and were degassed at low pressure. The final purity of these chemicals was ascertained by GLC (HP-8610) using FID, and the analysis indicated a mole fraction purity of 99.96 % in all cases. The purity of these chemicals was finally checked by comparing their density, viscosity and refractive index values with the available literature values Table 1 at the investigated temperatures. The agreement as shown in Table 1 was found to be satisfactory.

Binary liquid mixtures were prepared in thoroughly washed and dried narrow mouthed weighing glass bottles, with ground-glass stoppers by mixing the component liquids by mass on an electronic balance (Mettler, AE 240 Switzerland) with precision of ± 0.01mg. The masses of the component liquids required for preparing the mixture of known composition were calculated before hand and then a pseudo-binary mixture of two particular components in a fixed weight fraction ratio was prepared each time. Extreme care was taken to minimize the preferential evaporation during the process. The mixtures were kept about one hour to attain thermal equilibrium before the experimental observations were taken. The uncertainty of the mole fraction thus estimated was found to be less than $\pm 1 \times 10^{-4}$. Densities of pure liquids and their binary mixtures were determined using a Rudolph research analytical digital densimeter (DDH-2910. USA). The instrument is equipped with a built-in solid state thermostat and a resident program with an accuracy of temperature of 303.15 K ± 0.03K. The uncertainty in density measurements of liquid mixtures was found to be $\pm 5 \times 10^{-4}$ g.cm$^{-3}$. The densimeter was calibrated at each required temperature using doubly distilled water and with air as a standard. The densities of both water and dry air at each measured temperature were exactly matched with the data reported in the user's manual supplied by manufacturer.

The viscosities of pure liquids and their mixtures were determined using an Ubbelhode viscometer at atmospheric pressure and at the required temperatures. The viscometer was immersed in a low temperature viscometer bath with temperature control to with in ± 0.01 K. The flow time of each sample was repeated a minimum of four times and the results were averaged. The flow times were accurate to ± 0.1s. The absolute viscosity was then calculated from the relation $\eta = v.\ \rho$. Where '$v$' is the kinematic viscosity and '$\rho$ ' is the density. The calibration of viscometer was carried out with doubly distilled water and benzene. The uncertainty in viscosity was estimated to be ± 0.005 mPa.s.

The Refractive indices of pure liquids and their mixtures were measured using a refractometer (RM40, Metteler Toledo, Switzerland) with an uncertainty of $\pm$ 0.0004. The instrument has built-in solid state thermostat of temperature range (5-100°C) with an uncertainty of ± 0.1°C. The calibration of the instrument was carried out with dry air and water at a specified temperature.

## 3. Results and Discussion

The experimental values of density ($\rho$), viscosity ($\eta$), refractive index ($n_D$) of pure liquids and their binary mixtures were used to calculate the excess or deviation properties ($V^E$, $\Delta\eta$, $\Delta G^E$, $\Delta R$) using the following relations

$$V^E = (x_1 M_1 + x_2 M_2) / \rho - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2) \tag{1}$$

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{2}$$

$$\Delta G^E = RT\,[\ln(\eta V) - (x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2))] \tag{3}$$

$$\Delta R = R_m - (x_1 R_1 + x_2 R_2) \tag{4}$$

where $M$, $\eta$, $V$, $R_m$ are molar mass, viscosity, molar volume, molar refraction of the binary mixtures respectively.

Table 2 shows the experimental values of density ($\rho$), excess volume ($V^E$), dynamic viscosity ($\eta$), and refractive index ($n_D$) of the studied binary mixtures at (303.15, 308.15, 313.15) K over the entire mole fraction ($x_1$) range of diethyl maleate. The dependence of $V^E$ on mole fraction $x_1$ is graphically represented in Fig 1. It is observed that the values of $V^E$ for all the studied systems are negative over the entire range of composition. These negative $V^E$ values decrease with increase in temperature for diethyl maleate + acetophenone, + cyclopentanone, and + 3-pentanone. While for diethyl maleate + cyclohexanone $V^E$ values increase with increase in temperature indicating the effect of temperature on $V^E$. The curves are symmetric with minima occurring at about $x_1 \approx 0.52$ indicating the formation of 1:1 complexes. The probable reason for these negative of $V^E$ values may be attributed to the packing of larger molecules leading to interstitial void spaces that can be filled by smaller molecules. Further these negative $V^E$ values may signify the dipole-dipole interactions involving in the component molecules. Fig 2 shows the deviation in viscosity ($\Delta\eta$) against the mole fraction ($x_1$). The $\Delta\eta$ are values are negative for the mixtures of acetophenone, cyclopentanone, and 3-pentanone. While for diethyl maleate + cyclohexanone the $\Delta\eta$ values are positive in the lower composition of ester ($x_1 < 0.28$), however as the composition of ester (diethyl maleate increases $x_1 > 0.28$) these values become negative. The magnitude of $\Delta\eta$ alter with increase in temperature indicating the effect of temperature on $\Delta\eta$. The negative $\Delta\eta$ values suggest that dispersion forces are dominant in the mixtures while the positive $\Delta\eta$ values indicate the presence of specific interaction between the component molecules (7, 8). The plots of the excess Gibb's free energy of activation of flow ($\Delta G^E$) against mole fraction ($x_1$) are displayed in Fig 3. It is observed that the values of $\Delta G^E$ exhibit positive deviations for mixtures of acetophenone, cyclopentanone, and 3-pentanone, while for diethyl maleate + cyclohexanone $\Delta G^E$ values are positive in the lower composition of diethyl maleate and become negative at higher composition of ester $x_1 > 0.4$. These $\Delta G^E$ values also indicate the effect of temperature, as these values found to either increase or decrease with raise in temperature. The positive trend in $\Delta G^E$ values indicates that the strength of the interaction in component molecules is weaker, while the negative values indicate the strong interactions. Fig 4 shows the deviation in molar refraction against the mole fraction of diethyl maleate. The $\Delta R$ values for systems of diethyl maleate + cyclopentanone, + cyclohexanone, and + 3-pentanone exhibit negative deviations, while for diethyl maleate + acetophenone the $\Delta R$ values exhibit positive deviations at all the studied temperatures. The negative values found to be decrease with the increase in temperature, where as the positive values increase with increase in temperature. The variation of $V^E$, $\Delta\eta$, $\Delta G^E$, and $\Delta R$ with mole fraction was fitted to the Redlich-Kister polynomial Eq (6) of the type

$$\Delta y = x_1 (1 - x_1) \sum_{i=0}^{n} \mathrm{A}_i (2 x_1 - 1)^i \qquad (5)$$

Where '$n$' is the number of estimated parameters. The coefficients $\mathrm{A}_i$ of equation (5) and the corresponding standard deviations ($\sigma$) obtained from the method of least square with equal weights assigned to each points are calculated. The standard deviation ($\sigma$) is defined as

$$\sigma(y) = [\Sigma (y_{\text{obs}} - y_{\text{cal}})^2 / (n - m)]^{1/2} \qquad (6)$$

Where '$n$' an '$m$' represented the number of experimental data points and that of estimated parameters respectively. The coefficients $\mathrm{A}_i$ and the standard deviations ($\sigma$) are given in Table 3.

## 4. Correlation of Mixture Viscosities

The correlation involves the viscosity models having interaction parameters. In this paper we have selected some of such models for correlation of experimental mixture viscosities. The equations related to these models are given by following expressions.

Grunberg-Nissan (9):

Grunerg-Nissan proposed the following relation for the measurements

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \qquad (7)$$

where $d_{12}$ is a parameter to the interchange energy which reflects the non-ideality of the system.

Eyring-Vanlaar (10):

Eyring absolute rate theory provides the following relation for the binary mixtures describing the dynamic viscosities

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + \Delta E / RT \quad (8)$$

The first part of the right hand side of the Eq (8) can be regarded as an ideal part, while ΔE represents the excess activation energy of viscous flow and can be considered as non-ideal part. For Vanlaar equation Schrodt and Akel (10) correlated ΔE / RT is using following equation

$$\Delta E / RT = [A_{21} x_1 x_2 / x_1 + A_{12} x_2] \quad (9)$$

Hence the final form of Eyring-Van Laar equation for binary mixture viscosity is

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + [A_{21} x_1 x_2 / x_1 + A_{12} x_2] \quad (10)$$

Heric-Brewer (11):

Heric-Brewer proposed following relation to correlate the mixture viscosities as

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_1) + \Delta_{12} \quad (11)$$

where $\Delta_{12} = x_1 x_2 [\gamma_{12} + \gamma_{21}(x_1 - x_2)]$ is a function representing the departure from an ideal non interacting system. The coefficient $\gamma_{12}$ and $\gamma_{21}$ could be determined from a least square analysis.

McAllister (Four-Body) (12):

McAllister four-body interaction model to correlate the kinematic viscosities of binary mixtures is given by

$$\begin{aligned}\ln v = {} & x_1^4 \ln v_1 + 4x_1^3 x_2 \ln v_{1112} + 6 x_1^2 x_2^2 \ln v_{1122} + 4 x_1 x_2^3 \ln v_{2221} + x_2^4 \ln v_2 - \ln[x_1 + (x_2 M_2/M_1)] \\ & + 4 x_1^3 x_2 \ln[\{3 + (M_2/M_1)\}/4] + 6x_1^2 x_2^2 \ln[\{1 + (M_2/M_1)\}/2] \\ & + 4x_1 x_2^3 \ln[\{1 + (3 M_2/M_1)\}/4] + x_2^4 \ln(M_2/M_1) \quad (12)\end{aligned}$$

where $v$, $v_1$, $v_2$ are the kinematic viscosities of binary mixtures and those of the pure components 1 and 2 respectively. $v_{1112}$, $v_{1122}$ and $v_{2221}$ are the model parameters which are obtained by non-linear regression. The predictive ability of Eqs (7, 10, 11 and 12) was tested by calculating the percentage standard deviation $\sigma$ (%) between the experimental and calculated viscosity values as

$$\sigma(\%) = \left( \frac{1}{n-k} \Sigma \left\{ \frac{100(\eta_{expt} - \eta_{cal})}{\eta_{expt}} \right\}^2 \right)^{½} \quad (13)$$

Where '$n$' represents the number of data points in each set and '$k$' the number of numerical coefficients in the equations. The values of parameters evaluated by using least square method and the percentage standard deviation $\sigma$ (%) obtained by using experimental viscosity data are given in Table 4.

It is observed that the values of $\sigma$ (%) for Grunberg-Nissan relation are in the range of 0.03 to 4.78 %, while for Eyring-Vanlaar $\sigma$ (%) values are in the range 0.06-2.35 %, and for Heric-Brewer 0.02-2.43 %. However for McAllister (four-body) of three parameters model the $\sigma$ (%) values are in the range 0.03-0.95 %. During the analysis of these results it was observed that the use of two parameters in an equation reduces the $\sigma$ (%) values significantly below that of single parameter equation. Consequently the use of three parameters in an equation further reduces the $\sigma$ (%) values. As the average $\sigma$ (%) values of the studied models of one, two and three parameters respectively in the range 1.25 %, 0.69 % and 0.26 %. Nevertheless it is observed that all the relations employed are effective for the correlation of mixture viscosities as the predicted values are within the experimental uncertainty. Finally it can be concluded that the reproducibility of mixture viscosities obtained by three parameter model of McAllister is more accurate than employing one and two parameter equations.

## 5. Refractive Index Mixing Rules

Prediction of refractive indices of binary liquid mixtures is essential for the determination of composition of binary liquid mixtures. The measured refractive index data were predicted using Lorentz-Lorentz (13, 14), Eykman (15), Weiner (13, 14), Heller (13, 14), Dale-Gladstone (16), Newton (17), and Eyring-John (18). The equations pertaining in these models have been reported earlier (3). The predictive ability of these models was tested by calculating average percentage deviation (APD) between experimental and calculated values by using the relation

$$\text{Average percentage deviation} = 100 \sum_{i=1}^{n} \mid n_{\mathrm{D\,exp}} - n_{\mathrm{D\,cal}} \mid / \mathrm{n} \qquad (14)$$

The values of average percentage deviation (APD) are given in Table 5. The mean APD values for the present study are 0.138, 0.314, 0.083, 0.270, 0.260, 0.252, and 0.267 for Lorentz-Lorentz, Eykman, Weiner, Heller, Dale-Gladstone, Newton and Eyring-John respectively. It is observed that Weiner model predicted the lowest APD while Eykman model predicted highest APD values while other models except Lorentz-Lorentz showed nearly equal fitting ability. It can be concluded that this study indicates that all the studied theoretical mixing rules are interpreted in a simple quantitative manner and perform well within the limits of experimental errors.

## 6. Application of Prigogine-Flory-Patterson (PFP) Theory

The Prigogine-Flory-Patterson (PFP) theory (19-23) is used in our present study to correlate the $V^{\mathrm{E}}$ results for the present mixtures. The PFP theory leads to the following expression for $V^{\mathrm{E}}$

$$\frac{V_m^E}{(x_1V_1^* + x_2V_2^*)} = [(\tilde{v}^{\,1/3} - 1)\, \tilde{v}^{\,2/3}\, \psi_1\, \theta_2 (\chi_{12}/P_1^*)]/\, [(4/3)\, \tilde{v}^{\,-1/3} -1] - [(\tilde{v}_1 - \tilde{v}_2)^2\, (14/9)\, \tilde{v}^{\,-1/3}\, \psi_1\, \psi_2\,] / [(4/3)$$
$$(\tilde{v}^{\,-1/3} -1)\tilde{v}\,] + [(\tilde{v}_1 - \tilde{v}_2)\,(P_1^* - P_2^*)\psi_1\, \psi_2\,] / [\,P_1^*\, \psi_2 + P_2^*\, \psi_1\,] \qquad (15)$$

In the above relation the first term relates to the interactional contribution $V^E_{\mathrm{(int)}}$, the second term is the free volume contribution $V^E_{\mathrm{(fv)}}$, and the last term relates to the internal pressure contribution $V^E_{\mathrm{(ip).}}$ $\psi$, $\theta$ and $P^*$ are the molecular contact energy fraction, molecular surface fraction and characteristic pressure respectively. The parameters involved in Eq (15) for pure components are obtained through PFP theory are given in Table 6. An analysis of each of the three theoretical contributions to $V^E$ along with $\chi_{12}$ for the studied binary mixtures at (303.15, 308.15 and 313.15) K are given in Table 7. It is observed that though PFP theory includes three contributions for $V^E$, all these contributions are not contributing predominately. However the only significant contribution to $V^E$ is related with the interactional contribution $V^E_{\mathrm{(int)}}$ and interaction parameter $\chi_{12}$. A close observation of the values reported in Table 7 reveal that both interactional and free volume contributions are positive; while the internal pressure contribution is negative at all the studied temperatures. Also the $\chi_{12}$ values are negative except for diethyl maleate + acetophenone mixtures. From the analysis of PFP theory it can be concluded that the agreement between the experimental and the theoretical $V^E$ values at equimolar composition is satisfactory.

## 7. Conclusion

The density, viscosity and refractive index measurements for binary mixture of diethyl maleate + acetophenone, + cyclopenatnone, + 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 $\Delta G^{\ E}$ have been obtained. The reported excess properties show both positive and negative deviations. These excess properties were correlated by Redlich-Kister polynomial equation to derive the coefficients and standard deviations. Viscosity results were also analyzed by using empirical relations proposed by Grunberg-Nissan, Eyring-Vanlaar, Heric-Bewer and McAllister equations. Further the refractive indices of binary mixtures were correlated by using the various empirical / semi empirical relations. The Prigogine-Flory-Patterson (PFP) theory applied to the excess volume data correctly predicts the sign of $V^E$ values for all the studied mixtures. The PFP theory predicts the $V^E$ values satisfactorily for all the studied binary mixtures. For viscosity data McAllister (four-body) model shows excellent fitting ability than one and two parameter models. The refractive indices data for binary mixtures were correlated theoretically from pure component data by using the various mixing rules. It was observed that all the mixing rules predict the refractive indices reasonably well.

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**Table 1 Comparison of Experimental Densities ( $\rho$), Viscosities ( $\eta$), and Refractive Indices ($n_D$ ) of Pure Components with Available Literature Values at (303.15, 308.15 and 313.15) K**

| | $T$ /K | $\rho$/(g.cm$^{-3}$) | | $\eta$ /(mPa.s) | | $n_D$ | |
|---|---|---|---|---|---|---|---|
| Liquid | | Experimental | Literature | Experimental | Literature | Experimental | Literature |
| Diethyl Maleate | 298.15 | | | 3.142$^a$ | 3.140 [24] | | |
| | 303.15 | 1.0589 | 1.0587 [24] | 2.942 | | 1.4369 | 1.4366 [24] |
| | 308.15 | 1.0539 | 1.0537 [24] | 2.469 | | 1.4351 | 1.4349 [24] |
| | 313.15 | 1.0490 | 1.0487 [24] | 2.220 | | 1.4334 | 1.4332 [24] |
| Acetophenone | 303.15 | 1.0199 | 1.0194 [25] | 1.518 | 1.511 [24] | 1.5294 | 1.5297 [24] |
| | 308.15 | 1.0169 | 1.0172 [24] | 1.378 | | 1.5270 | |
| | 313.15 | 1.0135 | 1.0139 [24] | 1.291 | | 1.5250 | |
| Cyclopentanone | 303.15 | 0.9385 | 0.9390 [24] | 0.999 | 0.995 [24] | 1.4335 | |
| | 308.15 | 0.9339 | | 0.927 | | 1.4310 | |
| | 313.15 | 0.9290 | | 0.865 | | 1.4290 | |
| Cyclohexanone | 303.15 | 0.9377 | 0.9376 [24] | 1.816 | 1.810 [24] | 1.4465 | 1.4463 [26] |
| | 308.15 | 0.9328 | | 1.657 | 1.635 [26] | 1.4440 | 1.4439 [26] |
| | 313.15 | 0.9282 | | 1.542 | | 1.4420 | |
| 3-Pentanone | 303.15 | 0.8057 | 0.8054 [24] | 0.429 | 0.424 [24] | 1.3879 | 1.3878 [24] |
| | 308.15 | 0.8017 | | 0.397 | | 1.3857 | |
| | 313.15 | 0.7977 | | 0.388 | 0.380 [24] | 1.3835 | |

[a] Measured and compared at 298.15K

**Table 2 Mole Fraction ($x_1$), Densities ($\rho$), Excess Volumes ($V^E$), Dynamic Viscosities ($\eta$), Refractive Index ($n_D$) for the Binary Mixtures**

| $x_1$ | $\rho$ / g.cm$^{-3}$ | $V^E$/ cm$^3$.mol$^{-1}$ | $\eta$ / mPa.s | $n_D$ |
|---|---|---|---|---|
| | | Diethyl Maleate (1) + Acetophenone (2)<br>$T$=303.15 K | | |
| 0.0000 | 1.0199 | | 1.518 | 1.5294 |
| 0.0743 | 1.0255 | -0.202 | 1.592 | 1.5227 |
| 0.1222 | 1.0288 | -0.313 | 1.643 | 1.5190 |
| 0.2335 | 1.0355 | -0.502 | 1.768 | 1.5102 |
| 0.3222 | 1.0399 | -0.578 | 1.875 | 1.5034 |
| 0.4202 | 1.0441 | -0.615 | 2.002 | 1.4948 |
| 0.5215 | 1.0479 | -0.616 | 2.141 | 1.4855 |
| 0.6315 | 1.0513 | -0.554 | 2.303 | 1.4750 |
| 0.7228 | 1.0536 | -0.453 | 2.446 | 1.4656 |
| 0.8278 | 1.0558 | -0.295 | 2.622 | 1.4545 |
| 0.9216 | 1.0576 | -0.145 | 2.791 | 1.4441 |
| 1.0000 | 1.0589 | | 2.942 | 1.4369 |
| | | Diethyl Maleate (1) + Acetophenone (2)<br>$T$=308.15 K | | |
| 0.0000 | 1.0169 | | 1.378 | 1.5270 |
| 0.0743 | 1.0213 | -0.084 | 1.436 | 1.5205 |
| 0.1222 | 1.0239 | -0.124 | 1.476 | 1.5165 |
| 0.2335 | 1.0296 | -0.217 | 1.576 | 1.5077 |
| 0.3222 | 1.0336 | -0.260 | 1.662 | 1.5007 |
| 0.4202 | 1.0375 | -0.275 | 1.761 | 1.4928 |
| 0.5215 | 1.0412 | -0.280 | 1.870 | 1.4835 |
| 0.6315 | 1.0448 | -0.264 | 1.992 | 1.4731 |
| 0.7228 | 1.0474 | -0.221 | 2.099 | 1.4637 |
| 0.8278 | 1.0501 | -0.154 | 2.231 | 1.4529 |
| 0.9216 | 1.0523 | -0.083 | 2.358 | 1.4428 |
| 1.0000 | 1.0539 | | 2.469 | 1.4351 |
| | | Diethyl Maleate (1) + Acetophenone (2)<br>$T$=313.15 K | | |
| 0.0000 | 1.0135 | | 1.291 | 1.5250 |
| 0.0743 | 1.0173 | -0.030 | 1.352 | 1.5186 |
| 0.1222 | 1.0196 | -0.044 | 1.393 | 1.5147 |
| 0.2335 | 1.0246 | -0.072 | 1.488 | 1.5057 |
| 0.3222 | 1.0283 | -0.092 | 1.567 | 1.4990 |
| 0.4202 | 1.0321 | -0.109 | 1.656 | 1.4912 |
| 0.5215 | 1.0357 | -0.117 | 1.752 | 1.4822 |
| 0.6315 | 1.0392 | -0.103 | 1.857 | 1.4716 |

| | | | | |
|---|---|---|---|---|
| 0.7228 | 1.0418 | -0.073 | 1.946 | 1.4623 |
| 0.8278 | 1.0447 | -0.050 | 2.050 | 1.4515 |
| 0.9216 | 1.0471 | -0.024 | 2.144 | 1.4411 |
| 1.0000 | 1.0490 | | 2.220 | 1.4334 |
| | | Diethyl Maleate (1) + Cyclopentanone (2)<br>$T$=303.15 K | | |
| 0.0000 | 0.9385 | | 0.999 | 1.4335 |
| 0.0748 | 0.9567 | -0.278 | 1.109 | 1.4338 |
| 0.1564 | 0.9736 | -0.498 | 1.238 | 1.4341 |
| 0.2537 | 0.9906 | -0.674 | 1.400 | 1.4344 |
| 0.3526 | 1.0053 | -0.799 | 1.580 | 1.4348 |
| 0.4558 | 1.0183 | -0.868 | 1.775 | 1.4351 |
| 0.5615 | 1.0294 | -0.854 | 1.985 | 1.4355 |
| 0.6487 | 1.0371 | -0.776 | 2.164 | 1.4358 |
| 0.7589 | 1.0453 | -0.602 | 2.399 | 1.4361 |
| 0.8316 | 1.0500 | -0.457 | 2.559 | 1.4364 |
| 0.9335 | 1.0557 | -0.202 | 2.788 | 1.4367 |
| 1.0000 | 1.0589 | | 2.942 | 1.4369 |
| | | Diethyl Maleate (1) + Cyclopentanone (2)<br>$T$=308.15 K | | |
| 0.0000 | 0.9339 | | 0.927 | 1.4310 |
| 0.0748 | 0.9515 | -0.226 | 1.032 | 1.4319 |
| 0.1564 | 0.9682 | -0.430 | 1.151 | 1.4325 |
| 0.2537 | 0.9853 | -0.621 | 1.294 | 1.4330 |
| 0.3526 | 1.0000 | -0.750 | 1.443 | 1.4334 |
| 0.4558 | 1.0128 | -0.797 | 1.598 | 1.4337 |
| 0.5615 | 1.0239 | -0.784 | 1.762 | 1.4340 |
| 0.6487 | 1.0316 | -0.706 | 1.898 | 1.4343 |
| 0.7589 | 1.0399 | -0.544 | 2.072 | 1.4346 |
| 0.8316 | 1.0446 | -0.398 | 2.189 | 1.4348 |
| 0.9335 | 1.0504 | -0.156 | 2.355 | 1.4350 |
| 1.0000 | 1.0539 | | 2.469 | 1.4351 |
| | | Diethyl Maleate (1) + Cyclopentanone (2)<br>$T$=313.15 K | | |
| 0.0000 | 0.9290 | | 0.865 | 1.4290 |
| 0.0748 | 0.9461 | -0.179 | 0.962 | 1.4300 |
| 0.1564 | 0.9627 | -0.373 | 1.068 | 1.4307 |
| 0.2537 | 0.9799 | -0.574 | 1.197 | 1.4314 |
| 0.3526 | 0.9945 | -0.689 | 1.329 | 1.4317 |
| 0.4558 | 1.0074 | -0.746 | 1.469 | 1.4320 |
| 0.5615 | 1.0185 | -0.729 | 1.612 | 1.4323 |
| 0.6487 | 1.0262 | -0.647 | 1.732 | 1.4326 |
| 0.7589 | 1.0345 | -0.480 | 1.884 | 1.4328 |

| | | | | |
|---|---|---|---|---|
| 0.8316 | 1.0392 | -0.330 | 1.984 | 1.4330 |
| 0.9335 | 1.0452 | -0.112 | 2.127 | 1.4332 |
| 1.0000 | 1.0490 | | 2.220 | 1.4334 |

Diethyl Maleate (1) + Cyclohexanone (2)
$T$=303.15 K

| | | | | |
|---|---|---|---|---|
| 0.0000 | 0.9377 | | 1.816 | 1.4465 |
| 0.0662 | 0.9506 | -0.100 | 2.006 | 1.4455 |
| 0.1235 | 0.9612 | -0.202 | 2.098 | 1.4449 |
| 0.2857 | 0.9874 | -0.399 | 2.183 | 1.4432 |
| 0.3907 | 1.0021 | -0.498 | 2.226 | 1.4422 |
| 0.4985 | 1.0153 | -0.531 | 2.280 | 1.4412 |
| 0.5875 | 1.0247 | -0.477 | 2.346 | 1.4403 |
| 0.6769 | 1.0332 | -0.388 | 2.439 | 1.4394 |
| 0.7891 | 1.0429 | -0.258 | 2.576 | 1.4384 |
| 0.8763 | 1.0499 | -0.162 | 2.713 | 1.4378 |
| 0.9235 | 1.0534 | -0.095 | 2.802 | 1.4374 |
| 1.0000 | 1.0589 | | 2.942 | 1.4369 |

Diethyl Maleate (1) + Cyclohexanone (2)
$T$=308.15 K

| | | | | |
|---|---|---|---|---|
| 0.0000 | 0.9328 | | 1.657 | 1.4440 |
| 0.0662 | 0.9460 | -0.137 | 1.811 | 1.4434 |
| 0.1235 | 0.9566 | -0.242 | 1.882 | 1.4429 |
| 0.2857 | 0.9836 | -0.546 | 1.923 | 1.4419 |
| 0.3907 | 0.9984 | -0.664 | 1.934 | 1.4411 |
| 0.4985 | 1.0115 | -0.692 | 1.954 | 1.4401 |
| 0.5875 | 1.0210 | -0.657 | 1.989 | 1.4392 |
| 0.6769 | 1.0294 | -0.558 | 2.052 | 1.4382 |
| 0.7891 | 1.0387 | -0.376 | 2.163 | 1.4371 |
| 0.8763 | 1.0452 | -0.208 | 2.271 | 1.4362 |
| 0.9235 | 1.0487 | -0.141 | 2.347 | 1.4358 |
| 1.0000 | 1.0539 | | 2.469 | 1.4351 |

Diethyl Maleate (1) + Cyclohexanone (2)
$T$=313.15 K

| | | | | |
|---|---|---|---|---|
| 0.0000 | 0.9282 | | 1.542 | 1.4420 |
| 0.0662 | 0.9416 | -0.166 | 1.672 | 1.4417 |
| 0.1235 | 0.9524 | -0.299 | 1.726 | 1.4414 |
| 0.2857 | 0.9796 | -0.641 | 1.756 | 1.4406 |
| 0.3907 | 0.9944 | -0.768 | 1.753 | 1.4398 |
| 0.4985 | 1.0078 | -0.844 | 1.756 | 1.4390 |
| 0.5875 | 1.0174 | -0.829 | 1.784 | 1.4382 |
| 0.6769 | 1.0259 | -0.752 | 1.832 | 1.4373 |
| 0.7891 | 1.0350 | -0.549 | 1.917 | 1.4360 |
| 0.8763 | 1.0413 | -0.357 | 2.029 | 1.4350 |

| | | | | |
|---|---|---|---|---|
| 0.9235 | 1.0442 | -0.202 | 2.095 | 1.4343 |
| 1.0000 | 1.0490 | | 2.220 | 1.4334 |

Diethyl Maleate (1) + 3-Pentanone (2)

*T*=303.15 K

| | | | | |
|---|---|---|---|---|
| 0.0000 | 0.8057 | | 0.429 | 1.3879 |
| 0.0689 | 0.8328 | -0.197 | 0.495 | 1.3922 |
| 0.1248 | 0.8533 | -0.330 | 0.555 | 1.3954 |
| 0.2155 | 0.8841 | -0.509 | 0.671 | 1.4003 |
| 0.3053 | 0.9117 | -0.619 | 0.808 | 1.4050 |
| 0.3952 | 0.9371 | -0.713 | 0.970 | 1.4095 |
| 0.5012 | 0.9639 | -0.719 | 1.189 | 1.4145 |
| 0.6089 | 0.9883 | -0.652 | 1.454 | 1.4192 |
| 0.7089 | 1.0087 | -0.526 | 1.739 | 1.4236 |
| 0.8132 | 1.0280 | -0.344 | 2.099 | 1.4284 |
| 0.9155 | 1.0456 | -0.179 | 2.528 | 1.4335 |
| 1.0000 | 1.0589 | | 2.942 | 1.4369 |

Diethyl Maleate (1) + 3-Pentanone (2)

*T*=308.15 K

| | | | | |
|---|---|---|---|---|
| 0.0000 | 0.8017 | | 0.397 | 1.3857 |
| 0.0689 | 0.8284 | -0.160 | 0.453 | 1.3904 |
| 0.1248 | 0.8487 | -0.277 | 0.506 | 1.3939 |
| 0.2155 | 0.8792 | -0.434 | 0.605 | 1.3988 |
| 0.3053 | 0.9066 | -0.532 | 0.717 | 1.4033 |
| 0.3952 | 0.9314 | -0.556 | 0.850 | 1.4077 |
| 0.5012 | 0.9581 | -0.560 | 1.032 | 1.4127 |
| 0.6089 | 0.9826 | -0.517 | 1.248 | 1.4177 |
| 0.7089 | 1.0032 | -0.428 | 1.487 | 1.4224 |
| 0.8132 | 1.0228 | -0.299 | 1.782 | 1.4273 |
| 0.9155 | 1.0404 | -0.142 | 2.130 | 1.4320 |
| 1.0000 | 1.0539 | | 2.469 | 1.4351 |

Diethyl Maleate (1) + 3-Pentanone (2)

*T*=313.15 K

| | | | | |
|---|---|---|---|---|
| 0.0000 | 0.7977 | | 0.388 | 1.3835 |
| 0.0689 | 0.8240 | -0.121 | 0.439 | 1.3883 |
| 0.1248 | 0.8440 | -0.208 | 0.487 | 1.3919 |
| 0.2155 | 0.8741 | -0.326 | 0.575 | 1.3971 |
| 0.3053 | 0.9011 | -0.382 | 0.676 | 1.4019 |
| 0.3952 | 0.9259 | -0.418 | 0.793 | 1.4067 |
| 0.5012 | 0.9525 | -0.418 | 0.954 | 1.4119 |

| | | | | |
|---|---|---|---|---|
| 0.6089 | 0.9770 | -0.384 | 1.147 | 1.4169 |
| 0.7089 | 0.9976 | -0.303 | 1.359 | 1.4214 |
| 0.8132 | 1.0174 | -0.210 | 1.618 | 1.4259 |
| 0.9155 | 1.0352 | -0.090 | 1.925 | 1.4303 |
| 1.0000 | 1.0490 | | 2.220 | 1.4334 |

**Table 3 Derived Parameters of Eq (5) for various functions and standard deviation of the Binary Mixtures at (303.15, 308.15 and 313.15) K**

| Function | $T$/K | $A_o$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| | | | Diethyl Maleate (1) + Acetophenone (2) | | | |
| $V^E$ | 303.15 | -2.4827 | 0.4520 | 0.0103 | 0.2437 | 0.007 |
| | 308.15 | -1.1352 | 0.1069 | -0.0382 | -0.0838 | 0.005 |
| | 313.15 | -0.4481 | 0.0075 | 0.1653 | 0.0901 | 0.005 |
| $\Delta\eta$ | 303.15 | -0.4768 | -0.0440 | -0.0365 | -0.0075 | 0.001 |
| | 308.15 | -0.3116 | -0.0305 | -0.0551 | 0.0245 | 0.001 |
| | 313.15 | -0.1023 | 0.0244 | 0.0112 | -0.0014 | 0.001 |
| $\Delta G^E$ | 303.15 | 73.6542 | 12.2228 | -40.7641 | 7.6118 | 0.330 |
| | 308.15 | 120.5236 | -6.7229 | -85.1187 | 44.9859 | 0.858 |
| | 313.15 | 355.3952 | -3.1078 | 15.8483 | -4.9075 | 0.375 |
| $\Delta R$ | 303.15 | 2.9205 | 0.5101 | -1.2964 | -0.2759 | 0.019 |
| | 308.15 | 3.2889 | 0.5026 | -1.1381 | -0.2256 | 0.010 |
| | 313.15 | 3.6130 | 0.6371 | -1.1347 | -0.3973 | 0.014 |
| | | | Diethyl Maleate (1) + Cyclopentanone (2) | | | |
| $V^E$ | 303.15 | -3.4583 | 0.1353 | -0.0866 | 0.4880 | 0.008 |
| | 308.15 | -3.2175 | 0.2524 | 0.3789 | 0.1902 | 0.004 |
| | 313.15 | -3.0164 | 0.3075 | 0.9328 | 0.1657 | 0.009 |
| $\Delta\eta$ | 303.15 | -0.4360 | 0.0757 | -0.0287 | -0.0170 | 0.001 |
| | 308.15 | -0.1246 | -0.0035 | -0.0312 | -0.0185 | 0.001 |
| | 313.15 | -0.0591 | 0.0071 | -0.0158 | -0.0125 | 0.000 |
| $\Delta G^E$ | 303.15 | 1201.7319 | -145.0662 | -35.9981 | 21.8490 | 1.283 |
| | 308.15 | 1376.6299 | -355.1772 | 59.2403 | -20.4889 | 1.308 |
| | 313.15 | 1408.9552 | -337.3526 | 100.5643 | -59.1054 | 0.801 |
| $\Delta R$ | 303.15 | -0.9968 | 0.0496 | 0.0321 | 0.1773 | 0.002 |
| | 308.15 | -0.7872 | -0.0174 | 0.2632 | 0.0197 | 0.001 |
| | 313.15 | -0.6960 | -0.0674 | 0.3505 | -0.0303 | 0.002 |
| | | | Diethyl Maleate (1) + Cyclohexanone (2) | | | |
| $V^E$ | 303.15 | -2.0499 | 0.3746 | 0.8162 | -0.2328 | 0.010 |
| | 308.15 | -2.7778 | 0.2711 | 1.1174 | -0.1345 | 0.008 |
| | 313.15 | -3.3766 | -0.4111 | 0.6939 | 0.2930 | 0.009 |
| $\Delta\eta$ | 303.15 | -0.4104 | -0.9386 | 1.1420 | -0.8287 | 0.007 |
| | 308.15 | -0.4523 | -0.9790 | 1.0194 | -0.6360 | 0.005 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 313.15 | -0.5040 | -1.0118 | 0.7944 | -0.5222 | 0.005 |
| $\Delta G^E$ | 303.15 | 42.9065 | -978.6544 | 1593.6579 | -1200.7841 | 8.758 |
| | 308.15 | -186.8049 | -1198.7019 | 1610.6153 | -1010.007 | 7.552 |
| | 313.15 | -368.3131 | -1399.7055 | 1434.9773 | -854.6626 | 7.549 |
| $\Delta R$ | 303.15 | -0.3894 | 0.0293 | 0.0878 | 0.1397 | 0.002 |
| | 308.15 | -0.3114 | -0.0325 | 0.0624 | 0.1538 | 0.002 |
| | 313.15 | -0.2598 | 0.0010 | 0.0995 | 0.0083 | 0.001 |

Diethyl Maleate (1) + 3-Pentanone (2)

| | | | | | | |
|---|---|---|---|---|---|---|
| $V^E$ | 303.15 | -1.3530 | -0.4000 | -0.2003 | 0.0830 | 0.001 |
| | 308.15 | -1.3328 | -0.4039 | -0.2151 | 0.1402 | 0.001 |
| | 313.15 | -1.3016 | -0.4107 | -0.2510 | 0.2635 | 0.001 |
| $\Delta\eta$ | 303.15 | -1.9987 | -0.5436 | -0.2585 | -0.0348 | 0.002 |
| | 308.15 | -1.6167 | -0.4459 | -0.1825 | -0.0225 | 0.001 |
| | 313.15 | -1.4119 | -0.3830 | -0.1370 | -0.0287 | 0.001 |
| $\Delta G^E$ | 303.15 | 962.7587 | -99.7841 | -596.3286 | 1135.9690 | 5.159 |
| | 308.15 | 1097.9641 | -115.2276 | -797.1745 | 2389.8616 | 3.559 |
| | 313.15 | 648.0209 | -89.8669 | -368.8292 | 875.1386 | 2.648 |
| $\Delta R$ | 303.15 | -1.4941 | -0.3995 | -0.0497 | -0.2140 | 0.001 |
| | 308.15 | -1.5200 | -0.3978 | -0.0043 | -0.3271 | 0.001 |
| | 313.15 | -1.3839 | -0.3929 | -0.1678 | 0.1299 | 0.001 |

**Table 4 Adjustable Parameters and Percentage Standard Deviation $\sigma$ (%) of several correlations for the Viscosities of Binary Mixtures**

| $T$/K | Grunberg-Nissan | | Eyring-Vanlaar | | | Heric-Brewer | | | McAllister four- body | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d_{12}$ | σ (%) | $A_{21}$ | $A_{12}$ | σ (%) | $\gamma_{12}$ | $\gamma_{21}$ | $\sigma$ (%) | $\nu_{1112}$ | $\nu_{1122}$ | $\nu_{2221}$ | $\sigma$ (%) |
| Diethyl Maleate (1) + Acetophenone (2) | | | | | | | | | | | | |
| 303.15 | -0.0072 | 0.07 | 11.3899 | 1.0011 | 0.06 | 0.0574 | -0.0027 | 0.05 | 2.4283 | 2.0315 | 1.7214 | 0.04 |
| 308.15 | -0.0023 | 0.14 | 11.1388 | 1.0008 | 0.13 | 0.0623 | 0.0003 | 0.13 | 2.0854 | 1.8022 | 1.5378 | 0.06 |
| 313.15 | 0.0876 | 0.03 | 11.0653 | 0.9996 | 0.10 | 0.1522 | -0.0047 | 0.02 | 1.9647 | 1.6890 | 1.4802 | 0.03 |
| Diethyl Maleate (1) + Cyclopentanone (2) | | | | | | | | | | | | |
| 303.15 | 0.3266 | 0.24 | 11.0855 | 0.9903 | 0.11 | 0.5804 | -0.0905 | 0.05 | 2.3253 | 1.8983 | 1.4615 | 0.06 |
| 308.15 | 0.3897 | 0.88 | 10.8255 | 0.9745 | 0.13 | 0.6440 | -0.1766 | 0.12 | 2.0134 | 1.6998 | 1.3893 | 0.05 |
| 313.15 | 0.3939 | 0.85 | 10.6708 | 0.9748 | 0.14 | 0.6482 | -0.1721 | 0.16 | 1.8486 | 1.5579 | 1.2976 | 0.05 |
| Diethyl Maleate (1) + Cyclohexanone (2) | | | | | | | | | | | | |
| 303.15 | 0.0038 | 4.31 | 10.9993 | 0.9092 | 2.35 | 0.1826 | -0.5538 | 2.43 | 2.5235 | 1.8212 | 2.7780 | 0.95 |
| 308.15 | -0.0836 | 4.59 | 10.6060 | 0.8983 | 2.27 | 0.0973 | -0.6034 | 2.37 | 2.0958 | 1.5556 | 2.4692 | 0.80 |
| 313.15 | -0.1604 | 4.78 | 10.3149 | 0.8882 | 1.96 | 0.0224 | -0.6496 | 2.08 | 1.8224 | 1.4340 | 2.2331 | 0.68 |
| Diethyl Maleate (1) + 3-Pentanone (2) | | | | | | | | | | | | |
| 303.15 | 0.1991 | 0.52 | 10.2266 | 0.9933 | 0.48 | 0.4357 | -0.0851 | 0.44 | 1.8220 | 1.3118 | 0.8061 | 0.19 |
| 308.15 | 0.1438 | 0.41 | 9.9250 | 0.9917 | 0.31 | 0.3802 | -0.0911 | 0.27 | 1.5660 | 1.1238 | 0.7293 | 0.14 |
| 313.15 | 0.0926 | 0.29 | 9.7692 | 0.9935 | 0.23 | 0.3293 | -0.0803 | 0.18 | 1.4398 | 1.0334 | 0.6955 | 0.08 |

**Table 5 Average Percentage Deviation (APD) in the Refractive Index from Different Mixing Relations**

| System | T /K | Lorentz-Lorentz | Eykman | Weiner | Heller | Dale-Gladstone | Newton | Eyring-John |
|---|---|---|---|---|---|---|---|---|
| | | APD | APD | APD | APD | APD | APD | APD |
| Diethyl Maleate (1) + Acetophenone (2) | 303.15 | 0.412 | 0.961 | 0.241 | 0.812 | 0.762 | 0.713 | 0.787 |
| | 308.15 | 0.410 | 0.961 | 0.240 | 0.811 | 0.760 | 0.712 | 0.786 |
| | 313.15 | 0.424 | 0.980 | 0.247 | 0.834 | 0.785 | 0.736 | 0.809 |
| Diethyl Maleate (1) + Cyclopentanone (2) | 303.15 | 0.012 | 0.023 | 0.007 | 0.023 | 0.023 | 0.023 | 0.029 |
| | 308.15 | 0.013 | 0.024 | 0.008 | 0.024 | 0.024 | 0.024 | 0.030 |
| | 313.15 | 0.017 | 0.033 | 0.010 | 0.031 | 0.032 | 0.032 | 0.040 |
| Diethyl Maleate (1) + Cyclohexanone (2) | 303.15 | 0.016 | 0.038 | 0.010 | 0.030 | 0.030 | 0.030 | 0.030 |
| | 308.15 | 0.046 | 0.110 | 0.028 | 0.088 | 0.080 | 0.088 | 0.086 |
| | 313.15 | 0.075 | 0.180 | 0.046 | 0.146 | 0.144 | 0.143 | 0.144 |
| Diethyl Maleate (1) + 3-Pentanone (2) | 303.15 | 0.101 | 0.197 | 0.066 | 0.193 | 0.205 | 0.219 | 0.197 |
| | 308.15 | 0.080 | 0.158 | 0.053 | 0.153 | 0.165 | 0.180 | 0.158 |
| | 313.15 | 0.051 | 0.103 | 0.036 | 0.098 | 0.111 | 0.124 | 0.103 |

**Table 6 Parameters of the Pure Components used in PFP theory calculations at (303.15, 308.15 and 313.15) K**

| Component | $T$/K | $10^4\ \alpha$ / K$^{-1}$ | $10^4\ K_T$ / MPa$^{-1}$ | $\tilde{v}$ | $P^*$ / J.cm$^{-3}$ | $V^*$ / cm$^3$.mol$^{-1}$ |
|---|---|---|---|---|---|---|
| Diethyl Maleate | 303.15 | 9.47 | 57.1 | 1.2400 | 77.31 | 131.13 |
| | 308.15 | 9.52 | 58.7 | 1.2444 | 77.39 | 131.29 |
| | 313.15 | 9.56 | 60.4 | 1.2485 | 77.26 | 131.46 |
| Acetophenone | 303.15 | 5.81 | 22.4 | 1.1574 | 105.32 | 101.79 |
| | 308.15 | 5.83 | 23.0 | 1.1602 | 105.13 | 101.84 |
| | 313.15 | 5.85 | 23.6 | 1.1630 | 104.98 | 101.94 |
| Cyclopentanone | 303.15 | 10.83 | 38.6 | 1.2681 | 136.77 | 70.68 |
| | 308.15 | 10.89 | 39.8 | 1.2729 | 136.61 | 70.76 |
| | 313.15 | 10.95 | 41.0 | 1.2777 | 136.53 | 70.87 |
| Cyclohexanone | 303.15 | 9.45 | 37.9 | 1.2396 | 116.15 | 84.44 |
| | 308.15 | 9.49 | 39.0 | 1.2438 | 115.99 | 84.60 |
| | 313.15 | 9.54 | 40.1 | 1.2481 | 116.06 | 84.72 |
| 3-Pentanone | 303.15 | 9.93 | 46.3 | 1.2497 | 101.54 | 85.54 |
| | 308.15 | 9.98 | 47.7 | 1.2541 | 101.40 | 85.66 |
| | 313.15 | 10.03 | 49.3 | 1.2586 | 100.92 | 85.79 |

**Table 7 Calculated Values of Three Contributions of the PFP Theory to Excess Volume at (303.15, 308.15 and 313.15) K**

| System | $T$/K | $\chi_{12}$ / J.cm$^{-3}$ | $V^E$/ cm$^3$.mol$^{-1}$ at equimolar concentration | | Calculated contributions / cm$^3$.mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | | | Experimental | PFP | Interactional $V^E_{(int)}$ | Free Volume $V^E_{(fv)}$ | $P^*$ effect $V^E_{(ip)}$ |
| Diethyl Maleate (1) + Acetophenone (2) | 303.15 | 4.2876 | -0.616 | -0.621 | 0.00079 | 0.00818 | -0.00052 |
| | 308.15 | 8.1385 | -0.280 | -0.285 | 0.00081 | 0.00850 | -0.00053 |
| | 313.15 | 10.1524 | -0.117 | -0.104 | 0.00083 | 0.00878 | -0.00056 |
| Diethyl Maleate (1) + Cyclopentanone (2) | 303.15 | -7.5411 | -0.868 | -0.871 | 0.00104 | 0.00095 | -0.00011 |
| | 308.15 | -.65585 | -0.797 | -0.793 | 0.00106 | 0.00099 | -0.00011 |
| | 313.15 | -5.6720 | -0.746 | -0.722 | 0.00109 | 0.00100 | -0.00012 |
| Diethyl Maleate (1) + Cyclohexanone (2) | 303.15 | -4.5064 | -0.531 | -0.485 | 0.00100 | $2.161 \times 10^{-7}$ | $-1.787 \times 10^{-8}$ |
| | 308.15 | -5.9387 | -0.692 | -0.656 | 0.00102 | $4.961 \times 10^{-7}$ | $-4.072 \times 10^{-8}$ |
| | 313.15 | -7.2334 | -0.844 | -0.820 | 0.00105 | $2.247 \times 10^{-7}$ | $-1.852 \times 10^{-8}$ |
| Diethyl Maleate (1) + 3-Pentanone (2) | 303.15 | -5.8719 | -0.719 | -0.708 | 0.00109 | 0.00011 | $-6.183 \times 10^{-6}$ |
| | 308.15 | -4.6282 | -0.560 | -0.575 | 0.00112 | 0.00011 | $-6.240 \times 10^{-6}$ |
| | 313.15 | -3.2846 | -0.418 | -0.424 | 0.00115 | 0.00012 | $-6.549 \times 10^{-6}$ |

## Figure Captions

**Fig. 1.** Excess Volume, $V^E$ as a function of Diethyl Maleate mole fraction, $x_1$
(Diethyl Maleate + acetophenone): (□), at 303.15 K; (◊), at 308.15 K; (Δ),
at 313.15 K. (Diethyl Maleate + cyclopentanone): (X), at 303.15 K; (✳),
at 308.15 K; (-), at 313.15 K. (Diethyl Maleate + cyclohexanone): (O),
at 303.15 K; (+), at 308.15 K; (■), at 313.15 K. (Diethyl Maleate +
3-pentanone):( )◆ at 303.15 K; (▲), at 308.15 K; (●), at 313.15 K.

**Fig .2.** Deviations in viscosity, $\Delta\eta$ as a function of Diethyl Maleate mole fraction, $x_1$
(Diethyl Maleate + acetophenone): (□), at 303.15 K; (◊), at 308.15 K; (Δ),
at 313.15 K. (Diethyl Maleate + cyclopentanone): (X), at 303.15 K; (✳),
at 308.15 K; (-), at 313.15 K. (Diethyl Maleate + cyclohexanone): (O),
at 303.15 K; (+), at 308.15 K; (■), at 313.15 K. (Diethyl Maleate +
3-pentanone):( ◆, at 303.15 K; (▲), at 308.15 K; (●), at 313.15 K.

**Fig. 3.** Excess Gibbs Energy, $\Delta G^E$ as a function of Diethyl Maleate mole fraction, $x_1$
(Diethyl Maleate + acetophenone): (□), at 303.15 K; (◊), at 308.15 K; (Δ),
at 313.15 K. (Diethyl Maleate+ cyclopentanone): (X), at 303.15 K; (✳),
at 308.15 K; (-), at 313.15 K. (Diethyl Maleate + cyclohexanone): (O),
at 303.15 K; (+), at 308.15 K; (■), at 313.15 K. (Diethyl Maleate +
3-pentanone):( )◆ at 303.15 K; (▲), at 308.15 K; (●), at 313.15 K.

**Fig. 4.** Deviation in molar refraction, $\Delta R$ as a function of Diethyl Maleate mole fraction, $x_1$
(Diethyl Maleate + acetophenone): (□), at 303.15 K; (◊), at 308.15 K; (Δ),
at 313.15 K. (Diethyl Maleate+ cyclopentanone): (X), at 303.15 K; (✳),
at 308.15 K; (-), at 313.15 K. (Diethyl Maleate + cyclohexanone): (O),
at 303.15 K; (+), at 308.15 K; (■), at 313.15 K. (Diethyl Maleate +
3-pentanone):( ◆, at 303.15 K; (▲), at 308.15 K; (●), at 313.15 K.

**Fig. 1:**

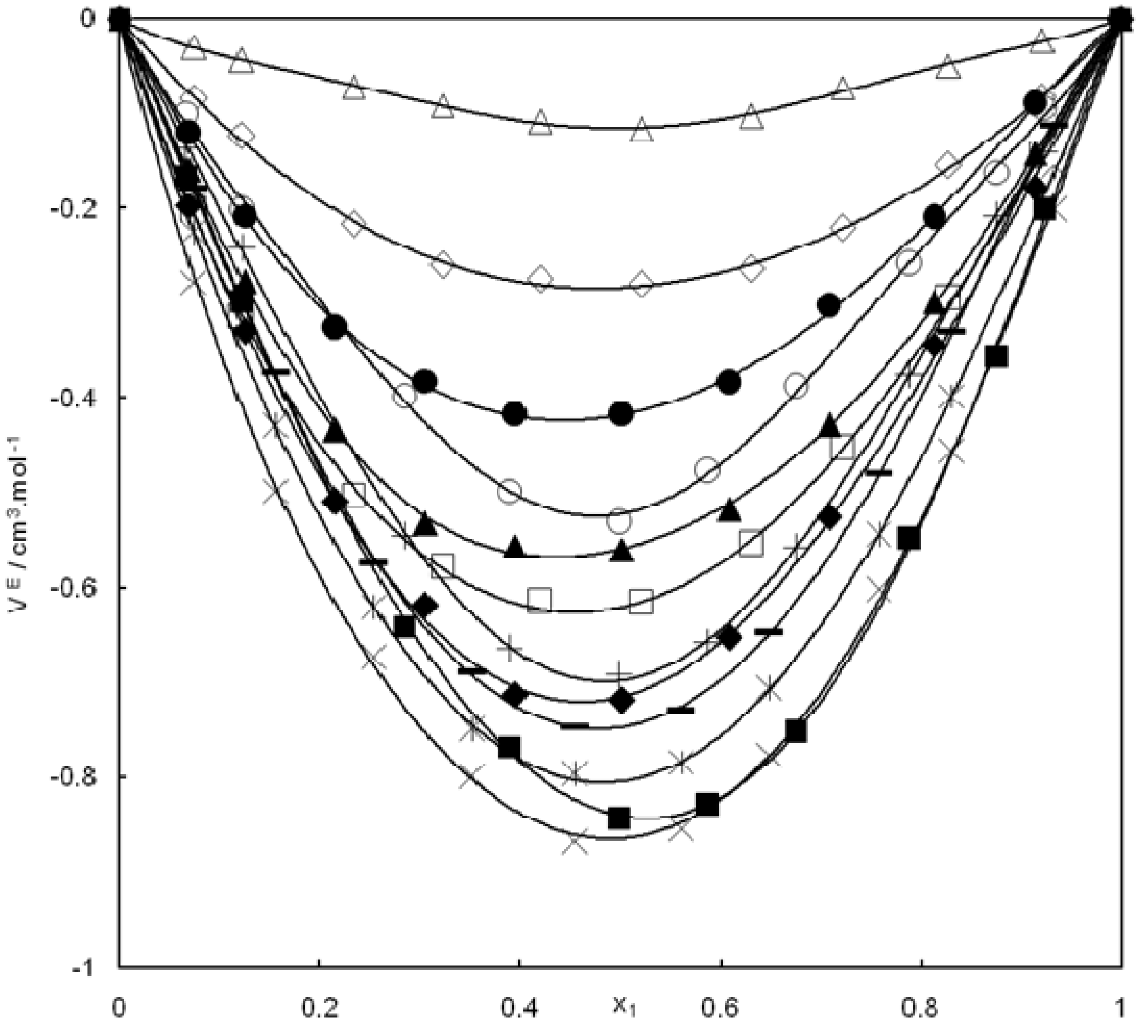

**Fig. 2:**

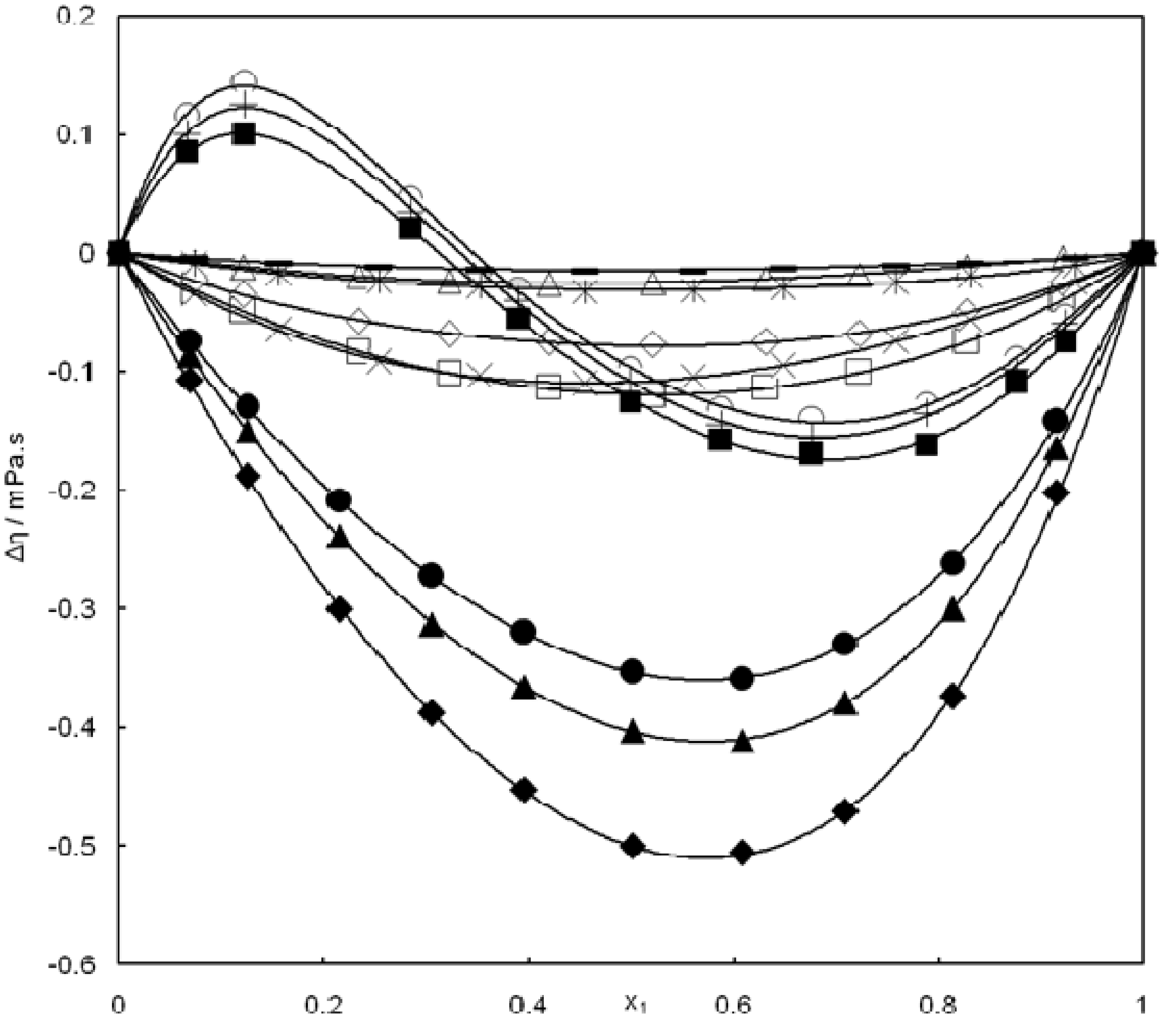

**Fig.3:**

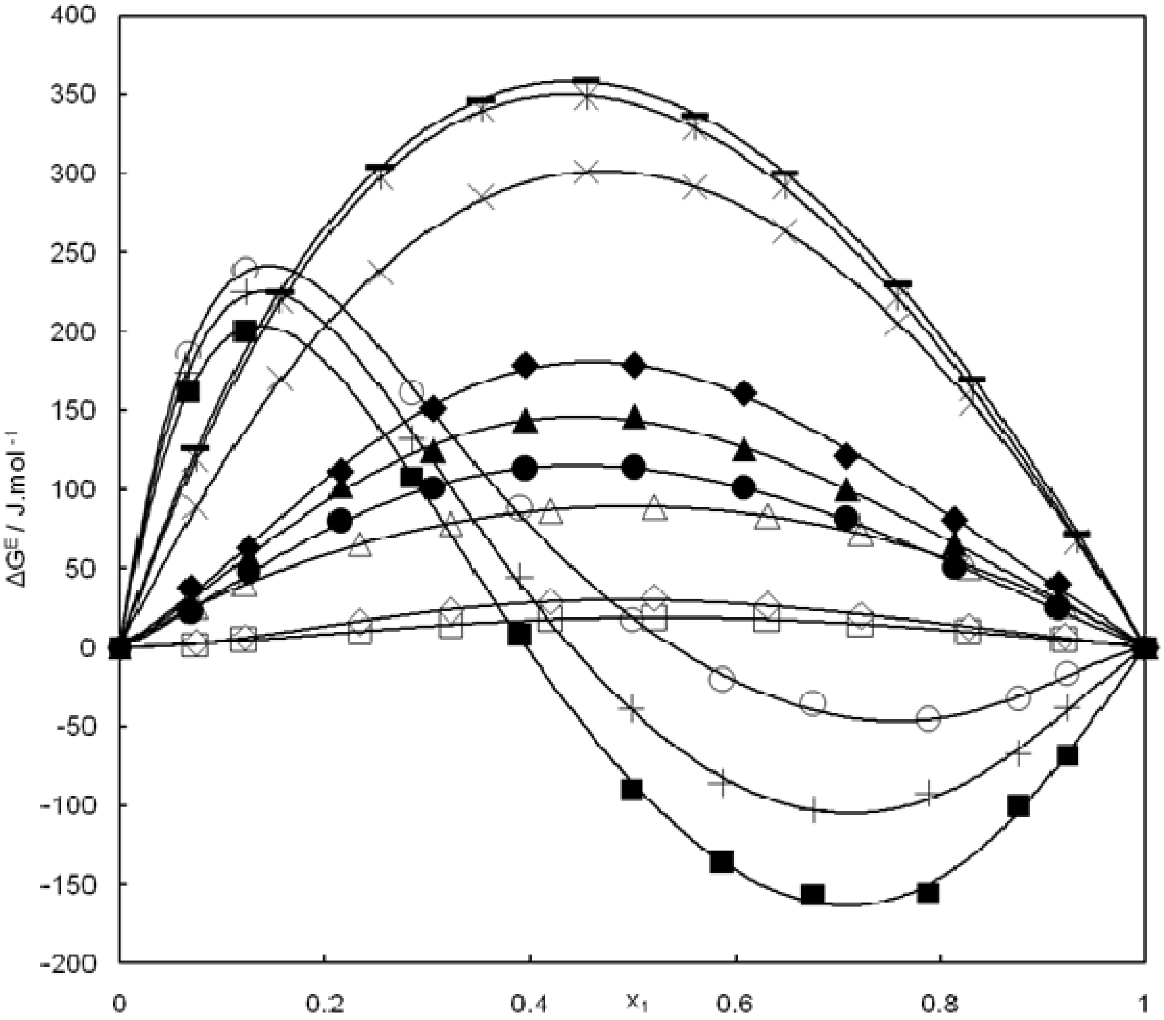
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
ΔG^E / J.mol^-1
0
0.2
0.4
x₁
0.6
0.8
1

**Fig.4:**