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

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Abstract

We have measured the density (), viscosity (), and refractive index (nD) at (303.15, 308.15, and 313.15) K for binary mixes of diethyl maleate with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone throughout the whole range of ester composition. The experimental data was used to derive values for the excess volume (VE), the excess viscosity (), the excess Gibbs free energy of activation of viscous flow (GE), and the excess molar refraction (R). Four body equations including Grunberg-Nissan, Eyring-Vanlaar, Heric-Brewer, and McAllister were used to establish relationships between the experimental viscosity data. We have evaluated the prognostic power of various refractive index mixing algorithms. The experimental surplus volume data at equimolar concentration has been further analyzed using the Prigogine-Flory-Patterson (PFP) theory.

Diethyl maleate, ketones, excess volume, and viscosity / density

Introduction

There are several chemical process businesses that cannot function without first studying the physico-chemical characteristics of multi-component mixtures. It has been discovered that studying the degree to which a liquid mixture deviates from ideal in terms of its physical properties is a great qualitative technique to extract information about the molecular structure and intermolecular forces present in the mixture. Diethyl maleate is an odorless, tasteless, and tasteless oily clear liquid. Its primary use is in the production of malathion, an organic phosphorous pesticide used extensively in agriculture, residential land and scalping, public recreation places, and public health pest control initiatives such the elimination of mosquitoes. The pharmaceutical and fragrance industries rely heavily on diethyl maleate intermediates.

To the best of our knowledge, a literature search has not turned up any information on the physicochemical characteristics of diethyl maleate binary mixes. Since our primary goal is to learn about the molecular interactions between diethyl maleate and ketones, this has led us to focus on diethyl maleate. At 298.15 K, liquid-liquid equilibrium (LLE) between water, carboxylic acid, and diethyl maleate ternary liquid systems has been found by Suheyla and Tugba (1). In this follow-up to our previous works (2-5), we present density, viscosity, and refractive index measurements at (303.15, 308.15, and 313.15) K for the binary mixtures of diethyl maleate and acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone across the full range of ester composition. Excess volumes (VE), viscosity deviation (), Gibbs free energy of activation of viscous flow excess (GE), and molar refraction deviation (R) have all been estimated from the experimental data. The binary coefficients and standard errors () were calculated by using multiparametric nonlinear regression analysis, which was then used to fit these parameters to the Redlich-Kister polynomial (6) equation. Empirical and semi-empirical correlations were used to establish a relationship between the viscosities of the binary mixes under investigation. Some mixing rule refractive index models were also used to make predictions based on the refractive index data, with the APD used to evaluate the accuracy of the predictions. Finally, the Prigogine-Flory-Patterson (PFP) hypothesis has been evaluated against the excess volume data at equimolar concentration.

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1. Experimental

The following chemicals were employed in this work without additional purification: diethyl maleate (Alfa-Aesar, > 98%), acetophenone (Sigma-Aldrich, > 99%), cyclopentanone, cyclohexanone, and 3-pentanone (Merck-India, > 99%). All the compounds were degassed at low pressure and kept on 0.4 nm molecular sieves for around 72 hours to remove any remaining water before use. GLC (HP- 8610) with FID was used to determine the ultimate purity of these substances, and the results showed a mole fraction purity of 99.96% in every instance. Finally, the density, viscosity, and refractive index values of these compounds at the temperatures under study were compared with the values reported in the literature (Table 1). Table 1 shows a good level of agreement.

Using an electronic balance (Mettler, AE 240 Switzerland) accurate to within 0.01mg, binary liquid solutions were made in cleaned and dried narrow mouth weighing glass vials with ground-glass stoppers. Each time, a pseudo-binary combination of two specific components in a defined weight fraction ratio was generated by first calculating the masses of the component liquids needed to make the mixture of known composition. Preferential evaporation was kept to a minimum by using stringent control measures. Before the experimental measurements were obtained, the mixes were left for roughly an hour to reach temperature equilibrium. The calculated mole fraction was determined to have an uncertainty of less than 1 x 10-4. The Rudolph research analytical digital densimeter (DDH-2910. USA) was used to measure the density of both pure liquids and binary mixes of those liquids. The device has a solid-state thermostat and an in-built software that can measure temperatures to within 0.03 degrees Kelvin. Density measurements of liquid mixes were found to have an error of less than 5 x 104 gcm-3. The densimeter was checked for accuracy against air and calibrated using double-distilled water at each of the specified temperatures. There was a one-to-one correspondence between the observed densities of water and dry air across all temperatures and the information provided in the manufacturer's instructions.

Ubbelhode viscometer readings were taken at standard atmospheric pressure and the specified temperatures to ascertain the pure liquid and mixed viscosities. The viscometer was submerged in a viscometer bath maintained at a low temperature within 0.01 K. At least four independent measurements of each sample's flow rate were averaged to create an overall average. The measured flow timings were precise to within 0.1s. Then, using the formula v = a, we were able to determine the absolute viscosity. Where "" is the density and "" is the kinematic viscosity. The viscometer was calibrated using benzene and double-distilled water. An error of 0.005 mPa.s was calculated for the value of the viscosity.

With an error of + 0.0004, a refractometer (RM40, Metteler Toledo, Switzerland) was used to determine the refractive index of both pure liquids and their mixes. The instrument's solid-state thermostat can measure temperatures from 5 to 100 degrees Celsius with a precision of 0.1 degrees Celsius. Dry air and water at a known temperature were used to calibrate the device.

2. Results and Discussion

The experimental values of density (ρ), viscosity (η), refractive index (n_D) of pure liquids and their binary mixtures were used to calculate the excess or deviation properties (V^E, $\Delta\eta$, ΔG^E, ΔR) 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, η, V, R_m are molar mass, viscosity, molar volume, molar refraction of the binary mixtures respectively.

Table 2 shows the experimental values of density (ρ), excess volume (V^E), dynamic viscosity (η), 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 valuesmay 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 thelower 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 plotsof the excess Gibb's free energy of activation of flow (ΔG^E) against mole fraction (x_1) are displayed in Fig 3. It is observed that the values of ΔG^E exhibit positive deviations for mixtures of acetophenone, cyclopentanone, and 3- pentanone, while for diethyl maleate + cyclohexanone ΔG^E values are positive in the lower composition of diethyl maleate and become negative at higher composition of ester $x_1 > 0.4$. These ΔG^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 ΔG^Evalues 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 ΔR values for systems of diethyl maleate + cyclopentanone, + cyclohexanone, and + 3-pentanone exhibit negative deviations, while for diethyl maleate + acetophenone the ΔR values exhibit positive deviations at allthe 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, $\Delta\eta$, ΔG^E, and ΔR with mole fraction was fitted to the Redlich-Kister polynomial Eq (6) of the type

$$\Delta y = x_1 (1- x_1) \sum A_i (2 x_1 - 1)^i \qquad (5)$$

here 'n' is the number of estimated parameters. The coefficients A_i of equation (5) and the corresponding standard deviations (σ) obtained from the method of least square with equal weights assigned to each points are calculated. The standard deviation (σ) is defined as

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

Where 'n' an 'm' represented the number of experimental data points and that of estimated parameters respectively. The coefficients A_i and the standard deviations (σ) are given in Table 3.

3. 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

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

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 $\Delta E / RT$ is using following equation

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

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

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

Heric-Brewer (11):

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

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

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 γ_{12} and γ_{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

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

$$+ 4x_1 x_2^3 \ln[\{1 + (3 M_2/ M_1)\}/4] + x_2^4 \ln(M_2 / M_1) \qquad (12)$$

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 σ (%) between the experimental and calculated viscosity values as

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

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 σ (%) obtained by using experimental viscosity data are given in Table 4.

It is observed that the values of σ (%) for Grunberg-Nissan relation are in the range of 0.03 to 4.78 %, while for Eyring-Vanlaar σ (%) 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 σ (%) values are in the range 0.03-0.95 %. During the analysisof these results it was observed that the use of two parameters in an equation reduces the σ (%) values significantly below that of single parameter equation. Consequently the use of three parameters in an equation further reduces the σ (%) values. As the average σ (%) 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.

4. 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

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

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 equalfitting ability. It can be concluded that this study indicates that all the studied theoretical mixing rules are interpretedin a simple quantitative manner and perform well within the limits of experimental errors.

5. 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^E results for the present mixtures. The PFP theory leads to the following expression for V^E

$$\frac{V_m^E}{(x_1 V_1^* + x_2 V_2^*)} = [(\tilde{v}^{1/3} - 1) \tilde{v}^{2/3} \psi_1 \theta_2 (\chi_{12} / P_1^*)]/ [(4/3) \tilde{v}^{-1/3} -1] - [(\tilde{v}_1 - \tilde{v}_2)^2 (14/9) \tilde{v}^{-1/3} \psi_1 \psi_2] / [(4/3) (\tilde{v}^{-1/3} -1) \tilde{v}] + [(\tilde{v}_1 - \tilde{v}_2) (P_1^* - P_2^*)\psi_1 \psi_2] / [P_1^* \psi_2 + P_2^* \psi_1] \qquad (15)$$

In the above relation the first term relates to the interactional contribution $V^E_{(int)}$, the second term is the free volume contribution $V^E_{(fv)}$, and the last term relates to the internal pressure contribution $V^E_{(ip)}$. ψ, θ 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 χ_{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 $V^E_{(int)}$ and interaction parameter χ_{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 χ_{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.

6. Conclusion

Over a wide range of concentrations, we measured the density, viscosity, and refractive index of a binary combination of diethyl maleate and acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone at (303.15), (308.15), and (313.15) K. The experimental data has been used to calculate the excess Gibb's free energy of activation of flow G E, the molar refraction R, and the excess volume VE. Both positive and negative deviations may be seen in the stated excess characteristics. The coefficients and standard deviations of these extra qualities were calculated using the Redlich-Kister polynomial equation. Empirical relations for viscosity calculated using the Grunberg-Nissan, Eyring-Vanlaar, Heric-Bewer, and McAllister equations were also studied. In addition, several empirical and semiempirical relations were used to establish a correlation between the refractive indices of binary mixes. The sign of VE values is accurately predicted by the Prigogine-Flory-Patterson (PFP) theory when applied to the excess volume data for all the investigated mixes. All of the investigated binary mixes have VE values that can be predicted successfully using the PFP theory. When it comes to viscosity data, the McAllister (four-body) model outperforms one- and two-parameter models in terms of how well they match the data. Theoretical correlations between the refractive indices of pure substances and those of binary mixtures

 data components by using a number of blending procedures. All mixing rules were found to be relatively accurate in predicting the refractive indices.

Table 1 Comparison of Experimental Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Pure Components with Available Literature Values at (303.15, 308.15 and 313.15) K

Liquid	T /K	ρ/(g.cm^{-3}) Experimental	Literature	η /(mPa.s) Experimental	Literature	n_D 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	

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[a] Measured and compared at 298.15K

Table 2 Mole Fraction (x_1), Densities (ρ), Excess Volumes (V^E), Dynamic Viscosities (η), Refractive Index (n_D) for the Binary Mixtures

x_1	ρ / g.cm^{-3}	V^E/ cm^3.mol^{-1}	η / mPa.s	n_D
		Diethyl Maleate (1) + Acetophenone (2)		
		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)		
		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)		
		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)
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)
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)

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=313.15 K

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
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

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

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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	σ
		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
ΔG^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
ΔR	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

ΔG^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
ΔR	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) + 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
ΔG^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
ΔR	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

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
Δn	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
ΔG^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
ΔR	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

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table 4 Adjustable Parameters and Percentage Standard Deviation σ (%) 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 (%)	γ_{12}	γ_{21}	σ (%)	v_{1112}	v_{1122}	v_{2221}	σ (%)
					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

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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) +	303.15	0.412	0.961	0.241	0.812	0.762	0.713	0.787
Acetophenone (2)	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) +	303.15	0.012	0.023	0.007	0.023	0.023	0.023	0.029
Cyclopentanone (2)	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) +	303.15	0.016	0.038	0.010	0.030	0.030	0.030	0.030
Cyclohexanone (2)	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) +	303.15	0.101	0.197	0.066	0.193	0.205	0.219	0.197
3-Pentanone (2)	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

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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	χ_{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) +	303.15	4.2876	-0.616	-0.621	0.00079	0.00818	-0.00052
Acetophenone (2)	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) +	303.15	-7.5411	-0.868	-0.871	0.00104	0.00095	-0.00011
Cyclopentanone (2)	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) +	303.15	-4.5064	-0.531	-0.485	0.00100	2.161×10^{-7}	-1.787×10^{-8}
Cyclohexanone (2)	308.15	-5.9387	-0.692	-0.656	0.00102	4.961×10^{-7}	-4.072×10^{-8}
	313.15	-7.2334	-0.844	-0.820	0.00105	2.247×10^{-7}	-1.852×10^{-8}
Diethyl Maleate (1) +	303.15	-5.8719	-0.719	-0.708	0.00109	0.00011	-6.183×10^{-6}
3-Pentanone (2)	308.15	-4.6282	-0.560	-0.575	0.00112	0.00011	-6.240×10^{-6}
	313.15	-3.2846	-0.418	-0.424	0.00115	0.00012	-6.549×10^{-6}

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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, Δη 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, ΔG^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, Δ𝑅 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: