Densities, Viscosities, and Refractive Indices of Binary Mixtures of Diethyl Oxalate with Some Ketones at (303.15, 308.15, and 313.15) K

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Densities, viscosities, and refractive indices of binary liquid mixtures of diethyl oxalate (DEO) with four ketones (acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone) were determined over the complete concentration range at (303.15, 308.15, and 313.15) K. The experimental values of mixtures and pure liquids have been used to calculate the excess molar volumes, deviations in viscosity, and deviations in molar refractions. These excess or deviation properties were fitted to the Redlich−Kister type equation. The refractive index and density values of the mixtures were used to test the accuracy of some of the available refractive index mixing relationships in predicting the binary refractive index data. Viscosity results were also analyzed by using the McAllister four-body interaction model to correlate the kinematic viscosities of binary liquid mixtures.

Introduction

The physicochemical properties of binary mixtures have been studied for several reasons, one of the most important of which is that these properties provide information about molecular interactions. Further such data obtained have wide applications in solution theory and molecular dynamics. Ketone is a class of chemical compound containing the carbonyl group in which the carbon atom is covalently bonded to an oxygen atom. Ketones are important intermediates in the synthesis of many organic compounds such as alkoxides, hydroxyalkynes, phosphine oxides, and cyanohydrins. Among the various ketones, acetophenone is used to create fragrances that resemble jasmine. It is used in chewing gum. Diethyl oxalate (DEO) is an important solvent with various applications in biochemistry and material science. Kenealy et al.[1] developed processes to treat wood chips with DEO at elevated temperatures with water and heat. A fundamental understanding of the mixture behavior and the molecular interactions of ketones with esters is therefore essential from the chemical and pharmaceutical point of view. A literature survey reveals that only a few studies on thermodynamic and transport properties[2−11] of binary mixtures consisting of either ketones or DEO as a common component are available. However, extensive studies on physical properties of these liquids are still lacking. Therefore, in continuation of our earlier work on physical property data of binary mixtures comprising esters with hydrocarbons,[12−15] in this paper we present the density, viscosity, and refractive index data of binary mixtures of DEO with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone over the entire range of composition and at (303.15, 308.15, and 313.15) K. From the experimental data the excess molar volume V^E, deviations in viscosity $\Delta\eta$, and deviation in molar refractivity ΔR have been computed. The applicability of some of the available mixing rules (Lorentz−Lorentz, Weiner, Newton, Dale−Gladstone, Eykman, Heller, and Eyring−John) in literature[16−21] has been studied. The viscosity equation of McAllister's four-body interaction model[22] has also been used to correlate the kinematic viscosities of binary liquid mixtures with mole fractions.

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

		$\rho/(g\cdot cm^{-3})$		$\eta/(mPa\cdot s)$		n_D	
liquid	T/K	exptl	lit.	exptl	lit.	exptl	lit.
DEO	303.15	1.0661	1.0669[30]	1.623	1.618[30]	1.4063	1.4061[31]
	308.15	1.0605	1.0607[31]	1.480		1.4040	1.4039[31]
	313.15	1.0545		1.367		1.4020	
acetophenone	303.15	1.0199	1.0194[32]	1.518	1.511[30]	1.5294	1.5297[30]
	308.15	1.0169	1.0150[32]	1.378		1.5270	
	313.15	1.0135	1.0106[32]	1.291		1.5250	
cyclopentanone	303.15	0.9385	0.9390[30]	0.999	0.995[30]	1.4352[a]	1.4354[a]
						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[30]	1.816	1.810[30]	1.4465	1.4463[3]
	308.15	0.9328		1.657	1.635[3]	1.4440	1.4439[3]
	313.15	0.9282		1.542		1.4420	
3-pentanone	303.15	0.8057	0.8054[30]	0.429	0.424[30]	1.3879	1.3878[30]
	308.15	0.8017		0.397		1.3857	
	313.15	0.7977		0.388	0.380[30]	1.3835	

[a] Measured and compared at 298.15 K with ref 30.

Experimental Section

DEO, 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 mole fraction purity of > 99.0 %. Experimental results of density, viscosity, and the refractive index of pure liquids at 303.15 K are compared in Table 1 with the published data.

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 ± 0.0001 g. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots via a syringe into stoppered bottles. The

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uncertainty in mole fraction was thus estimated to be less than ± 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. Densities of pure liquids and their mixtures were measured using a DMA-35 Anton Paar digital densimeter with an uncertainty of 0.1 %. Viscosities were determined using an Ubbelhode viscometer. The time of efflux of a constant volume of liquid through the capillary was measured with the help of a precalibrated RACER stopwatch corrected to ± 0.1 s. The viscometer was always kept in a vertical position in a water thermostat at the required temperature. The viscosity was calculated from measured efflux time t, using the following relation

$$\eta = \rho(At - B/t) \tag{1}$$

where ρ is the density and A and B are the characteristic constants of the viscometer, which were determined by taking water and benzene as the calibrating liquids. The uncertainty in viscosity thus estimated was found to be ± 0.9 %. Refractive indices were measured using a refractometer (RM40, Metteler Toledo, Switzerland) with an uncertainty of ± 0.0001. The instrument has a built-in solid state thermostat temperature range of (5 to 100) °C with an uncertainty of ± 0.1 °C. The instrument calibration was carried out with doubly distilled water. An average of three measurements was taken for each sample.

Results and Discussion

Table 2 lists the experimental values of densities, ρ, excess molar volumes, V^E, viscosities, η, and refractive indices, n_D, of binary liquid mixtures of DEO with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone at (303.15, 308.15, and 313.15) K. The density, ρ, values have been used to calculate the excess molar volumes, V^E, using the following equation

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{2}$$

where ρ is the density of the mixture and (x_1, M_1, and ρ_1) and (x_2, M_2, and ρ_2) are the mole fraction, molar mass, and density of pure components 1 and 2, respectively.

The viscosity deviations, $\Delta\eta$, were calculated by using the equation

$$\Delta\eta/\text{mPa}\cdot\text{s} = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where η is the absolute viscosity of the binary mixture and η_1 and η_2 are the viscosities of the pure components.

The refractive index values have been used to calculate the Lorentz−Lorentz molar refraction,[23] and deviations in the molar refraction have been calculated as

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = R_m - (x_1R_1 + x_2R_2) \tag{4}$$

where R_m is the molar refractivity of mixtures and R_1 and R_2 are the molar refractivities of pure components 1 and 2, respectively.

All of the quantities (V^E, $\Delta\eta$, and ΔR) have been fitted to the Redlich−Kister[24] polynomial equation by the method of least-squares to derive binary coefficients A_0, A_1, and A_2.

$$\Delta y = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \tag{5}$$

The variation in standard deviation (σ) was calculated using the relation

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

where n represents the number of data points and m is the number of coefficients. The calculated values of A_0, A_1, and A_2 along with the standard deviations (σ) are given in Table 3.

Excess molar volumes for the mixtures of DEO with studied ketones (acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone) at (303.15, 308.15, and 313.15) K are represented in Figure 1. It is observed that for DEO + acetophenone, + cyclopentanone, and + cyclohexanone the V^E values are positive over the entire composition range, while for DEO + 3-pentanone they are negative, and the magnitude of negative V^E values increases with the increase in temperature. Similarly, for mixtures of DEO + cyclopentanone and + cyclohexanone the V^E increase with the increase in temperature. However, for DEO + acetophenone the V^E decrease with the increase in temperature. The maxima or minima of each isotherm fall around the mole fraction $x_1 = 0.5$, indicating the formation of 1:1 adducts in all systems studied. The V^E is the resultant contribution from several opposing effects, namely, chemical, physical, and structural. The chemical or specific interactions result in volume contractions, leading to negative excess volume, and these include charge transfer and complex-forming interactions. The physical interactions or nonspecific interactions are weak and hence contribute a positive V^E, while the structural contributions are mostly negative and arise from several effects such as interstitial accommodation and the geometrical fitting of one component into another due to the differences in the free volume and molar volume between components.

In our present study the negative V^E may be due to the structural difference (interstitial accommodation) of the component liquids. The dipole moment of DEO ($\mu = 2.49$), acetophenone ($\mu = 2.95$), cyclopentanone ($\mu = 2.86$), cyclohexanone ($\mu = 3.08$), and 3-pentanone ($\mu = 2.82$) are all similar, so one would expect dipole−dipole interactions between DEO and ketones to be of same strength and hence its corresponding contributions to the excess functions to be almost similar. However, Figures 1 and 2 reveal that the magnitude of V^E and $\Delta\eta$ for these mixtures differs considerably.

A correlation between the sign of $\Delta\eta$ and V^E has been observed for a number of binary solvent systems. If $\Delta\eta$ is positive, then V^E is negative or vice versa.[25] In our present study the isotherms of V^E and $\Delta\eta$ do not obey the above general statement. Therefore, it may be considered that the strength of the specific or dispersion forces is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular size and shapes of the components are also equally responsible. Rastogi et al.[26] suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-interaction part in the form of the size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter.

Table 2. Values of Density ρ, Excess Volume V^E, Viscosity η, and Refractive Index n_D for the Binary Liquid Mixtures

x_1	$\frac{\rho}{\mathrm{g\cdot cm^{-3}}}$	$\frac{V^E}{\mathrm{cm^{-3}\cdot mol^{-1}}}$	$\frac{\eta}{\mathrm{mPa\cdot s}}$	n_D	x_1	$\frac{\rho}{\mathrm{g\cdot cm^{-3}}}$	$\frac{V^E}{\mathrm{cm^{-3}\cdot mol^{-1}}}$	$\frac{\eta}{\mathrm{mPa\cdot s}}$	n_D
DEO (1) + Acetophenone (2)									
$T = 303.15$ K									
0.0000	1.0199		1.518	1.5294	0.5501	1.0440	0.373	1.655	1.4574
0.0875	1.0241	0.051	1.557	1.5171	0.6601	1.0493	0.327	1.657	1.4439
0.1478	1.0267	0.113	1.578	1.5087	0.7601	1.0543	0.244	1.654	1.4325
0.2538	1.0312	0.214	1.610	1.4945	0.8846	1.0606	0.107	1.648	1.4187
0.3443	1.0349	0.303	1.628	1.4826	0.9500	1.0638	0.038	1.635	1.4117
0.4591	1.0399	0.360	1.645	1.4685	1.0000	1.0661		1.623	1.4063
$T = 308.15$ K									
0.0000	1.0169		1.378	1.5270	0.5501	1.0401	0.301	1.477	1.4560
0.0875	1.0210	0.034	1.405	1.5151	0.6601	1.0452	0.244	1.485	1.4424
0.1478	1.0236	0.075	1.418	1.5068	0.7601	1.0498	0.179	1.487	1.4309
0.2538	1.0279	0.166	1.439	1.4928	0.8846	1.0556	0.066	1.489	1.4167
0.3443	1.0315	0.237	1.454	1.4811	0.9500	1.0585	0.015	1.490	1.4095
0.4591	1.0362	0.293	1.467	1.4671	1.0000	1.0605		1.480	1.4040
$T = 313.15$ K									
0.0000	1.0135		1.291	1.5250	0.5501	1.0357	0.241	1.362	1.4544
0.0875	1.0174	0.028	1.308	1.5133	0.6601	1.0402	0.223	1.366	1.4411
0.1478	1.0199	0.061	1.317	1.5053	0.7601	1.0445	0.164	1.370	1.4293
0.2538	1.0240	0.141	1.333	1.4912	0.8846	1.0499	0.063	1.373	1.4154
0.3443	1.0275	0.195	1.344	1.4796	0.9500	1.0525	0.031	1.375	1.4079
0.4591	1.0320	0.238	1.355	1.4656	1.0000	1.0545		1.367	1.4020
DEO (1) + Cyclopentanone (2)									
$T = 303.15$ K									
0.0000	0.9385		0.999	1.4335	0.5509	1.0207	0.117	1.326	1.4139
0.0679	0.9509	0.038	1.045	1.4299	0.6587	1.0329	0.106	1.394	1.4115
0.1501	0.9650	0.064	1.095	1.4264	0.7587	1.0434	0.088	1.458	1.4098
0.2518	0.9810	0.089	1.153	1.4226	0.8755	1.0549	0.043	1.537	1.4080
0.3903	1.0006	0.111	1.233	1.4182	0.9610	1.0627	0.013	1.596	1.4068
0.4511	1.0085	0.117	1.265	1.4164	1.0000	1.0661		1.623	1.4063
$T = 308.15$ K									
0.0000	0.9339		0.927	1.4310	0.5509	1.0153	0.136	1.207	1.4122
0.0679	0.9461	0.049	0.960	1.4278	0.6587	1.0274	0.127	1.269	1.4098
0.1501	0.9601	0.074	0.999	1.4244	0.7587	1.0379	0.099	1.329	1.4079
0.2518	0.9760	0.097	1.048	1.4207	0.8755	1.0493	0.054	1.401	1.4059
0.3903	0.9954	0.124	1.119	1.4164	0.9610	1.0570	0.029	1.454	1.4045
0.4511	1.0032	0.135	1.152	1.4147	1.0000	1.0605		1.480	1.4040
$T = 313.15$ K									
0.0000	0.9290		0.865	1.4290	0.5509	1.0097	0.137	1.107	1.4116
0.0679	0.9411	0.049	0.891	1.4262	0.6587	1.0217	0.127	1.163	1.4089
0.1501	0.9549	0.082	0.925	1.4231	0.7587	1.0321	0.099	1.219	1.4067
0.2518	0.9706	0.113	0.968	1.4198	0.8755	1.0433	0.067	1.288	1.4043
0.3903	0.9899	0.133	1.031	1.4158	0.9610	1.0510	0.034	1.342	1.4027
0.4511	0.9977	0.137	1.058	1.4142	1.0000	1.0545		1.367	1.4020
DEO (1) + Cyclohexanone (2)									
$T = 303.15$ K									
0.0000	0.9377		1.816	1.4465	0.5507	1.0151	0.207	1.584	1.4239
0.0784	0.9502	0.042	1.777	1.4429	0.6755	1.0303	0.165	1.575	1.4186
0.1495	0.9610	0.083	1.737	1.4399	0.7601	1.0402	0.120	1.581	1.4154
0.2501	0.9754	0.154	1.682	1.4359	0.8756	1.0531	0.055	1.606	1.4108
0.3443	0.9884	0.190	1.637	1.4323	0.9502	1.0610	0.020	1.620	1.4081
0.4324	1.0000	0.217	1.609	1.4287	1.0000	1.0661		1.623	1.4063
$T = 308.15$ K									
0.0000	0.9328		1.657	1.4440	0.5507	1.0096	0.230	1.415	1.4223
0.0784	0.9451	0.057	1.595	1.4406	0.6755	1.0247	0.190	1.404	1.4168
0.1495	0.9558	0.103	1.556	1.4376	0.7601	1.0345	0.151	1.407	1.4133
0.2501	0.9703	0.154	1.500	1.4340	0.8756	1.0474	0.077	1.437	1.4088
0.3443	0.9831	0.205	1.461	1.4307	0.9502	1.0553	0.037	1.464	1.4059
0.4324	0.9947	0.225	1.435	1.4273	1.0000	1.0605		1.480	1.4040
$T = 313.15$ K									
0.0000	0.9282		1.542	1.4420	0.5507	1.0040	0.252	1.285	1.4204
0.0784	0.9401	0.089	1.466	1.4388	0.6755	1.0190	0.204	1.276	1.4152
0.1495	0.9506	0.145	1.416	1.4359	0.7601	1.0287	0.164	1.284	1.4116
0.2501	0.9649	0.203	1.360	1.4321	0.8756	1.0414	0.097	1.329	1.4071
0.3443	0.9777	0.238	1.325	1.4287	0.9502	1.0493	0.045	1.351	1.4043
0.4324	0.9892	0.255	1.304	1.4252	1.0000	1.0545		1.367	1.4020

Table 2. Continued

x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^{-3} \cdot mol^{-1}$	η / $mPa \cdot s$	n_D	x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^{-3} \cdot mol^{-1}$	η / $mPa \cdot s$	n_D
				DEO (1) + 3-Pentanone (2)					
				T = 303.15 K					
0.0000	0.8057		0.429	1.3879	0.5325	0.9608	−0.068	0.916	1.3999
0.0865	0.8340	−0.014	0.485	1.3901	0.6518	0.9900	−0.061	1.071	1.4018
0.1436	0.8520	−0.029	0.527	1.3916	0.7587	1.0147	−0.045	1.224	1.4033
0.2448	0.8825	−0.044	0.610	1.3941	0.8659	1.0382	−0.021	1.395	1.4047
0.3389	0.9094	−0.054	0.701	1.3962	0.9438	1.0546	−0.007	1.525	1.4056
0.4495	0.9394	−0.065	0.818	1.3984	1.0000	1.0661		1.623	1.4063
				T = 308.15 K					
0.0000	0.8017		0.397	1.3857	0.5325	0.9561	−0.098	0.848	1.3983
0.0865	0.8299	−0.023	0.452	1.3881	0.6518	0.9851	−0.090	0.987	1.4000
0.1436	0.8478	−0.038	0.491	1.3897	0.7587	1.0096	−0.067	1.121	1.4014
0.2448	0.8782	−0.065	0.567	1.3924	0.8659	1.0329	−0.036	1.274	1.4026
0.3389	0.9050	−0.083	0.650	1.3947	0.9438	1.0491	−0.011	1.391	1.4034
0.4495	0.9348	−0.092	0.759	1.3969	1.0000	1.0605		1.480	1.4040
				T = 313.15 K					
0.0000	0.7977		0.388	1.3835	0.5325	0.9512	−0.131	0.808	1.3969
0.0865	0.8258	−0.036	0.440	1.3861	0.6518	0.9799	−0.114	0.936	1.3986
0.1436	0.8436	−0.056	0.478	1.3877	0.7587	1.0042	−0.091	1.061	1.3998
0.2448	0.8738	−0.086	0.551	1.3906	0.8659	1.0272	−0.046	1.196	1.4008
0.3389	0.9005	−0.117	0.627	1.3930	0.9438	1.0433	−0.024	1.295	1.4015
0.4495	0.9301	−0.129	0.726	1.3954	1.0000	1.0545		1.367	1.4020

Table 3. Fitting Parameters and Standard Deviations (σ) of Equation 6 for the Least-Squares Representation of Excess Properties

function	T/K	A_0	A_1	A_2	σ
		DEO (1) + Acetophenone (2)			
V^E	303.15	1.4778	0.1882	−0.9186	0.004
	308.15	1.1977	0.0992	−1.0281	0.005
	313.15	0.9918	0.1834	−0.7756	0.006
$\Delta\eta$	303.15	0.3049	−0.0368	0.0708	0.003
	308.15	0.1693	−0.0024	0.0713	0.002
	313.15	0.1132	0.0056	0.0393	0.002
ΔR	303.15	0.7947	−0.0223	−0.3576	0.009
	308.15	0.9857	−0.0209	−0.4087	0.011
	313.15	1.0661	0.0988	−0.0244	0.016
		DEO (1) + Cyclopentanone (2)			
V^E	303.15	0.4681	−0.0264	−0.0036	0.005
	308.15	0.5359	−0.0044	0.0654	0.007
	313.15	0.5469	−0.0356	0.1361	0.005
$\Delta\eta$	303.15	−0.0628	−0.0636	0.0721	0.001
	308.15	−0.1105	−0.0075	0.0401	0.001
	313.15	−0.1360	−0.0265	0.0010	0.001
ΔR	303.15	−0.3246	0.0371	−0.0368	0.005
	308.15	−0.1586	0.0276	0.0137	0.002
	313.15	0.3020	0.0178	0.1787	0.003
		DEO (1) + Cyclohexanone (2)			
V^E	303.15	0.8576	−0.0870	−0.5115	0.005
	308.15	0.9178	−0.0480	−0.3085	0.005
	313.15	1.0152	−0.1788	−0.0312	0.005
$\Delta\eta$	303.15	−0.5193	−0.0155	0.3045	0.004
	308.15	−0.5994	0.0280	0.0303	0.005
	313.15	−0.6615	0.0791	−0.0919	0.007
ΔR	303.15	0.8287	−0.0828	−0.4615	0.007
	308.15	1.0751	−0.0776	−0.6151	0.011
	313.15	1.0973	−0.0286	−0.1914	0.013
		DEO (1) + 3-Pentanone (2)			
V^E	303.15	−0.2695	−0.0005	0.1238	0.003
	308.15	−0.3740	−0.0174	0.0961	0.004
	313.15	−0.5111	0.0237	0.1525	0.005
$\Delta\eta$	303.15	−0.5990	−0.0019	0.0075	0.001
	308.15	−0.5085	−0.0159	−0.0218	0.001
	313.15	−0.4098	0.0393	0.0494	0.004
ΔR	303.15	0.2327	0.0003	−0.1093	0.002
	308.15	0.3918	−0.0531	−0.1900	0.004
	313.15	0.5307	0.0174	−0.2689	0.002

Figure 2 shows plots of $\Delta\eta$ versus the mole fraction of DEO. It is observed that for the binary mixture DEO + acetophenone the $\Delta\eta$ values are completely positive, while for cyclohexanone and 3-pentanone they are completely negative. However, for cyclopentanone the $\Delta\eta$ values exhibit both positive and negative deviations at 303.15 K, while at higher temperatures these values become completely negative. The magnitude of negative $\Delta\eta$ values increases with the increase in temperature for cyclopentanone and cyclohexanone systems. In case of 3-pentanone these negative values decrease with the increase in temperature. The positive deviation from the rectilinear dependence of viscosity on mole fraction and maxima[27,28] may occur if strong specific interactions cause complex formation. Negative deviations occur where dispersion forces are primarily responsible for interaction, but they may also occur where the components are known to interact more strongly. However, such information from viscosity composition diagrams might not be obtained in the case of mixtures where weak specific interactions are operative.

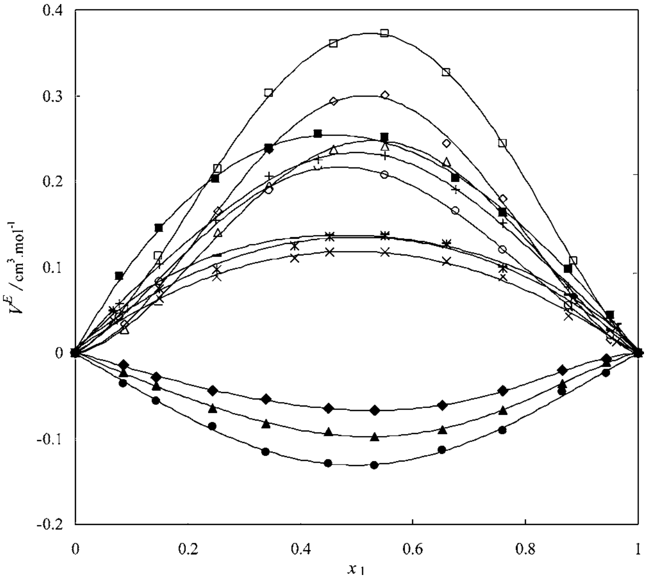

Figure 1. Excess volume, V^E, as a function of DEO mole fraction, x_1. (DEO + acetophenone): □, T = 303.15 K; ◇, T = 308.15 K; △, T = 313.15 K. (DEO + cyclopentanone): ×, T = 303.15 K; ∗, T = 308.15 K; −, T = 313.15 K. (DEO + cyclohexanone): ○, T = 303.15 K; +, T = 308.15 K; ■, T = 313.15 K. (DEO + 3-pentanone): ◆, T = 303.15 K; ▲, T = 308.15 K; ●, T = 313.15 K.

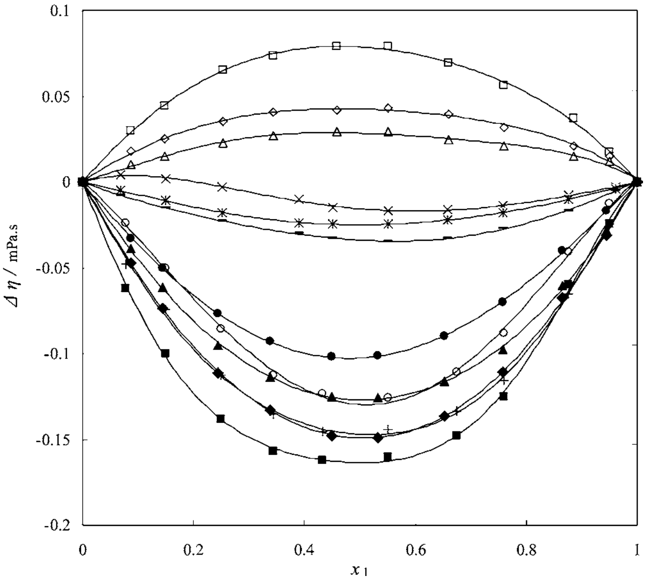

Figure 2. Deviation in viscosity, $\Delta\eta$, as a function of DEO mole fraction, x_1. (DEO + acetophenone): □, T = 303.15 K; ◇, T = 308.15 K; △, T = 313.15 K. (DEO + cyclopentanone): ×, T = 303.15 K; ∗, T = 308.15 K; −, T = 313.15 K. (DEO + cyclohexanone): ○, T = 303.15 K; +, T = 308.15 K; ■, T = 313.15 K. (DEO + 3-pentanone): ◆, T = 303.15 K; ▲, T = 308.15 K; ●, T = 313.15 K.

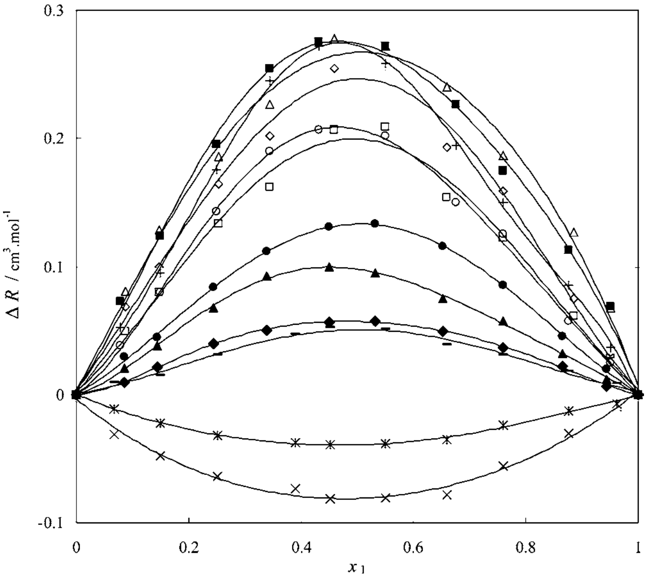

Figure 3. Deviation in molar refraction, ΔR, as a function of DEO mole fraction, x_1. (DEO + acetophenone): □, T = 303.15 K; ◇, T = 308.15 K; △, T = 313.15 K. (DEO + cyclopentanone): ×, T = 303.15 K; ∗, T = 308.15 K; −, T = 313.15 K. (DEO + cyclohexanone): ○, T = 303.15 K; +, T = 308.15 K; ■, T = 313.15 K. (DEO + 3-pentanone): ◆, T = 303.15 K; ▲, T = 308.15 K; ●, T = 313.15 K.

It is interesting to compare the present V^E and $\Delta\eta$ data at $x_1 = x_2 = 0.5$ with the few selected binary mixtures already reported in literature.[9−11] In the present study for the binary mixtures DEO + 3-pentanone both V^E and $\Delta\eta$ were found to be negative. A similar behavior has been observed for the binary mixtures 1,4-dioxane + DEO[10] at (298.15, 303.15, and 308.15) K, DEO + benzene,[11] and DEO + toluene.[11] This behavior is characteristic of mixture in which the molecular size and shapes of the components are also equally responsible, while the large positive values observed for DEO + cyclohexanone and DEO + acetophenone are similar to those observed for DEO + octan-1-ol[9] and DEO + decan-1-ol,[9] indicating physical or nonspecific interactions.

The deviations in molar refraction, ΔR, with mole fraction are displayed graphically in Figure 3. The ΔR values for DEO + acetophenone, cyclohexanone, and 3-pentanone are completely positive and increase with the increase in temperature, while in the case of cyclopentanone they are negative at (303.15 and 308.15) K, but these values exhibit positive deviations at 313.15 K. The positive deviations in ΔR values on mole fraction dependence are considered because of the presence of significant interactions in the mixtures, whereas negative deviations in ΔR values indicate strong interactions between the components of the mixtures.[29] In all figures the points represent the data calculated from eqs 2 to 4, while smooth curves are drawn from the best-fitted data calculated from eq 5.

Mixing Rules of Refractive Index. The applicability of various mixing rules for predicting the refractive indices of binary mixtures has been studied. The following mixing rules have been analyzed.

Lorentz−Lorentz:[16,17]

$$[n_{12}^2 - 1/n_{12}^2 + 2] = [n_1^2 - 1/n_1^2 + 2]\Phi_1 + [n_2^2 - 1/n_2^2 + 2]\Phi_2 \quad (7)$$

Weiner:[16,17]

$$[n_{12}^2 - n_1^2/n_{12}^2 + 2n_1^2] = [n_2^2 - n_1^2/n_2^2 + 2n_1^2]\Phi_2 \quad (8)$$

Newton:[18]

$$n_{12}^2 - 1 = (n_1^2 - 1)\Phi_1 + (n_2^2 - 1)\Phi_2 \quad (9)$$

Dale−Gladstone:[19]

$$n_{12} - 1 = (n_1 - 1)\Phi_1 + (n_2 - 1)\Phi_2 \quad (10)$$

Eykman:[20]

$$[n_{12}^2 - 1/n_{12} + 0.4] = [n_1^2 - 1/n_1 + 0.4]\Phi_1 + [n_2^2 - 1/n_2 + 0.4]\Phi_2 \quad (11)$$

Heller:[16,17]

$$[n_{12} - n_1/n_1] = 3/2[(n_2/n_1)^2 - 1/(n_2/n_1)^2 + 2]\Phi_2 \quad (12)$$

Eyring−John:[21]

$$n_{12} = n_1\Phi_1^2 + 2(n_1n_2)^{1/2}\Phi_1\Phi_2 + n_2\Phi_2^2 \quad (13)$$

In all of the above relations Φ_1 and Φ_2 are the volume fractions, and n_1 and n_2 are the refractive indices of pure components 1 and 2, respectively. n_{12} is the refractive index of the mixture.

The average deviation (AD) between the experimental and the calculated values is obtained by using the relation

$$\mathrm{AD} = \sum_{i=1}^{n} |n_\mathrm{D} - n_\mathrm{D,cal}|/n \qquad (14)$$

where n is the number of data points and n_D is the refractive index of the binary mixture. A comparison of all AD values for different mixing rules indicates that the Lorentz−Lorentz and Weiner relation gives very low deviations for all of the binary mixtures studied. A similar trend is observed for Newton and Eyring−John relations. Further, it is observed that most of the studied mixing relations show very low deviations (AD) at 303.15 K. However, at higher temperatures the magnitude of deviations is different for each model. For the systems DEO + acetophenone, + cyclohexanone, and + 3-pentanone the AD is increased with an increase in temperature, while for cyclopentanone the values of AD decrease with an increase in temperature. From the analysis of our present study, it can be concluded that the predicting ability of the various studied mixing rules is quite satisfactory at 303.15 K.

Viscosity Model. A number of viscosity models have been tested by several authors to correlate the mixture viscosities. In this work we have selected the McAllister[22] four-body interaction model to correlate the kinematic viscosities, since the McAllister four-body equation is a quartic equation having three interaction parameters. This model approaches more nearly a three-dimensional treatment, and the molecular diameter is greater than 1.5. The equation of this model applied to binary mixtures is given by

$$\begin{aligned}\ln \upsilon = {} & x_1^{\,4} \ln \upsilon_1 + 4x_1^{\,3}x_2 \ln \upsilon_{1112} + 6x_1^{\,2}x_2^{\,2} \ln \upsilon_{1122} + 4x_1 \times \\ & x_2^{\,3} \ln \upsilon_{2221} + x_2^{\,4} \ln \upsilon_2 - \ln[x_1 + (x_2M_2/M_1)] + 4x_1^{\,3}x_2 \times \\ & \ln[\{3 + M_2/M_1\}/4] + 6x_1^{\,2}x_2^{\,2} \ln[\{1 + M_2/M_1\}/2] + 4x_1x_2^{\,3} \times \\ & \ln[\{1 + 3(M_2/M)_1\}/4] + x_2^{\,4} \ln(M_2/M_1) \end{aligned} \qquad (15)$$

where ν, ν_1, and ν_2 are the kinematic viscosities of binary mixtures and the pure components 1 and 2, respectively. ν_{1112}, ν_{1122}, and ν_{2221} are the model parameters which are obtained by nonlinear regression. The correlating ability of eq 15 was tested by calculating the standard deviation σ between the experimental and the calculated viscosities as

$$\sigma = \left(\frac{1}{n-k}\sum\left\{\frac{(\nu_\mathrm{expt} - \nu_\mathrm{cal})^2}{\nu_\mathrm{expt}}\right\}^{1/2}\right) \qquad (16)$$

where n represents the number of data points in each set and k the number of numerical coefficients in the equations. Table 4 summarizes the model parameters along with standard deviations σ. The values of σ are in the range from $(5\text{ to }55)\cdot10^{-4}$ at 303.15 K, $(5\text{ to }50)\cdot10^{-4}$ at 308.15 K, and $(3\text{ to }62)\cdot10^{-4}$ at 313.15 K. However, of the binary mixtures studied, the McAllister model predicts very low σ values for DEO + cyclopentanone at all studied temperatures. The probable reason for these low values may be due to polarizability and the size and the shape of pure components. The dielectric constants of DEO, acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone are 1.8, 17.39, 13.60, 16.10, and 17.0, respectively.

Table 4. Adjustable Parameters and Standard Deviation σ of the McAllister Four-Body Model for the Viscosities of Binary Liquid Mixtures

		McAllister four-body model			
system	T/K	ν_{1112}	ν_{1122}	ν_{2221}	100 σ
DEO (1) + acetophenone (2)	303.15	1.5971	1.5817	1.6084	0.16
	308.15	1.4407	1.4420	1.4304	0.16
	313.15	1.3282	1.3126	1.3191	0.17
DEO (1) + cyclopentanone (2)	303.15	1.4521	1.3729	1.1387	0.05
	308.15	1.2881	1.7677	0.9878	0.05
	313.15	1.2047	1.1042	0.9342	0.03
DEO (1) + cyclohexanone (2)	303.15	1.5509	1.4309	1.6843	0.38
	308.15	1.3432	1.3512	1.4482	0.50
	313.15	1.2125	1.2580	1.2913	0.62
DEO (1) + 3-pentanone (2)	303.15	1.2574	0.9375	0.6079	0.55
	308.15	1.1424	0.8520	0.6074	0.45
	313.15	1.0998	0.7865	0.6134	0.45

Conclusion

It is realized that these binary data will have some relevance in industries because the ester studied is an important solvent with various applications in biochemistry and materials science, while ketones are important intermediates in the synthesis of many organic compounds. In this paper densities, viscosities, and refractive indices at (303.15, 308.15, and 313.15) K were measured over the entire range of mixture composition of DEO with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone. Out of these measured data the excess molar volume, deviation in viscosity, and molar refraction have been calculated and correlated by a Redlich−Kister type polynomial equation to derive the coefficients and standard deviation. Both negative and positive deviations are observed for the excess molar volume, V^E, deviation in viscosity, $\Delta\eta$, and molar refraction, ΔR. Viscosity results were also analyzed by using the McAllister four-body interaction model. Furthermore, the refractive indices of binary mixtures were correlated theoretically from pure component data by using the various empirical and semiempirical relations.

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Supporting Information Available:

ADs obtained from eqs 7 to 13 for mixing rules of refractive index at (303.15, 308.15, and 313.15) K. This material is available free of charge via the Internet at http://pubs.acs.org.

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