

## MOLECULAR INTERACTION STUDIES OF BINARY MIXTURES OF DIETHYL OXALATE WITH BUTYL VINYL ETHER, DIISOPROPYL ETHER, ANISOLE AND DIBUTYL ETHER IN TERMS OF THERMODYNAMIC, TRANSPORT AND ACOUSTIC PROPERTIES

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Viscosity, the speeds of sound and density were measured in the binary mixtures of diethyl oxalate with butyl vinyl ether, diisopropyl ether, anisole and dibutyl ether at  $T = 303.15, 308.15$  and  $313.15$  K. The experimental data were used to calculate the excess molar volume  $V_m^E$ , deviation in viscosity  $\Delta\eta$  and the acoustical parameters, namely isentropic compressibility ( $K_S$ ), free volume ( $V_f$ ), free length ( $L_f$ ) and internal pressure ( $\pi_i$ ). The excess or deviation properties were fitted to the Redlich-Kister polynomials and the results interpreted in terms of the molecular interactions present in mixtures. Theoretical viscosities were calculated using the Grunberg-Nissan, Lobe and Krishnan-Laddha models before their merits were studied in terms of interaction parameters.

**Keywords:** diethyl oxalate, density, viscosity, speeds of sound, isentropic compressibility

### 1. Introduction

Thermodynamic, transport and ultrasonic properties of liquid-liquid mixtures are essential theoretically and in terms of process design. Density, viscosity and speeds of sound as well as their excess or deviation properties are mostly useful in engineering design processes in addition to the chemical and biological industries [1]. The analysis of these properties provides detailed information on the intermolecular interactions present in the liquid mixtures. Further excess properties provide key values for calculating the properties of multicomponent mixtures from the data of pure components. They can also provide data to evaluate parameters characterizing interactions between unlike molecules.

Diethyl oxalate (DEO) is a colorless organic compound and the diethyl ester of oxalic acid. DEO is used in active pharmaceutical ingredients, polymers and intermediates for dyestuffs as well as a solvent to make esters, resins, fragrances and electronic lacquers. Tremendous growth has been seen in the pharmaceutical industry attributed to the high consumption of DEO. Demand for drugs such as steroids and barbiturates has led to an increase in the usage of DEO. While ethers are a class of organic compounds that contain an oxygen between two alkyl groups, they are relatively unreactive so are useful as solvents for fats, oils, waxes, perfumes, resins, dyes, gums and hydrocarbons. Vapors of certain

ethers are used as insecticides, mildewcides and fumigants for soil. These numerous applications of ethers have sparked the present study to know more about their possible molecular interactions when mixed with DEO.

A literature review uncovered several studies on the thermodynamic, transport and volumetric properties of binary mixtures of esters with different organic liquids [2]-[6]. Likewise, few studies have been undertaken on the density, viscosity and speeds of sound [7]-[11] of binary mixtures containing DEO with ethers as well as polar and non-polar solvents. However, it has been observed that to the best of our knowledge, except for the system of DEO with anisole (AS), no studies have been found in the literature concerning any of the other binary systems undertaken in our present study. The study of the thermodynamic and transport properties of binary mixtures containing esters with ethers contributes to the understanding of the theory of the liquid state [12]-[17]. In this paper, the densities, viscosities and speeds of sound of the binary mixtures of DEO with butyl vinyl ether (BVE), diisopropyl ether (DIPE), AS and dibutyl ether (DBE) at  $T = 303.15, 308.15$  and  $313.15$  K were reported. From the above experimental data, several excess or deviation parameters were evaluated at the respective temperatures which are important in industrial processes. These excess or deviation properties were fitted to the Redlich-Kister polynomial equation [18] to derive the binary coefficients and estimate the standard

Table 1: Chemical Specifications and Purity Estimation

Chemical	Source	Initial mole fraction purity	Purification method	Analysis method	Final mole fraction purity
DEO	Sigma-Aldrich	0.990	None	GC-8610	> 0.996
BVE	Sigma-Aldrich	0.980	Distillation	GC-8610	> 0.984
DIPE	Sigma-Aldrich	0.980	None	GC-8610	> 0.984
AS	Sigma-Aldrich	0.997	None	GC-8610	> 0.997
DBE	Sigma-Aldrich	0.993	Distillation	GC-8610	> 0.995

GC\* - Gas-liquid chromatography

errors. The experimental viscosity data were used to test correlations between viscosity models proposed by Grunberg-Nissan [22], Lobe [23] and Krishnan-Laddha [24].

## 2. Experimental

### 2.1. Materials

DEO, BVE, DIPE, AS and DBE all with a mass fraction purity of >0.990 were supplied by Sigma-Aldrich and purified by vacuum distillation. The filtrates of these chemicals were collected in dark bottles over molecular sieve 0.4 nm beads to remove any water then degassed just before their use. Gas chromatography (GC) detected no traceable amounts of impurities in the filtrates. The stated purities of these filtered chemicals and their final purities as estimated by GC (HP 8610) analysis are shown in Table 1.

### 2.2. Methods

The binary liquid mixtures were arranged by mixing known masses of pure liquids in airtight stoppered bottles. All mass measurements were made using a Mettler single-pan digital balance with an accuracy of  $\pm 0.01$  mg (AE240, Switzerland). The resulting mole fraction uncertainty was calculated to be less than  $1 \times 10^{-4}$ . The densities of the pure chemicals and their binary mixtures were fixed by using a density meter (Rudolph Research Analytical DDM 2910). The instrument contains a high-precision platinum thermometer in the density sensor to accurately measure the temperature. The instrument was calibrated frequently before each experiment was started using deionized double distilled water and dry air. The uncertainty in the densities was within  $0.0004 \text{ g}\cdot\text{cm}^{-3}$ . The viscosities of the pure liquids and their mixtures were measured by using a Ubbelohde viscometer [17]. The viscometer was calibrated using double distilled water. The uncertainty in the viscosities was estimated to be within  $0.10 \text{ mPa}\cdot\text{s}$ .

The speeds of sound of the pure liquids and liquid mixtures were calculated by using a Mittal Enterprises

model F-81 single-crystal variable path interferometer (New Delhi, India) operating at a frequency of 2 MHz and with an accuracy of  $\pm 0.01 \text{ ms}^{-1}$ . The instrument was calibrated by measuring the velocity in standard liquids, i.e. AR grade benzene and carbon tetrachloride. The estimated uncertainty in the speeds of sound was found to be within 1%. All measurements were taken at a constant temperature in an INSREF model IRI-016C constant low temperature bath (India) by circulating water from a thermostat around the cell containing the liquid.

## 3. Results and discussion

The experimental values of the density ( $\rho$ ), viscosity ( $\eta$ ), speeds of sound ( $U$ ) and isentropic compressibility ( $K_S$ ) were determined for the studied binary mixtures over the entire composition range expressed as a function  $x_i$  of DEO at 303.15, 308.15 and 313.15 K. A large number of data are not reported in this paper but are available from the editorial office of this journal.

From the density data, excess molar volumes ( $V_m^E$ ) and deviations in viscosity ( $\Delta\eta$ ) were calculated using the following relations:

$$V_m^E = (x_1M_1 + x_2M_2)/\rho_{12} - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad (1)$$

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

where  $x$ ,  $M$ ,  $\eta$  and  $\rho$  are the mole fraction, molar mass, viscosity and density, respectively, of the pure components 1 and 2.  $\rho_{12}$  denotes the density and  $\eta_{12}$  the viscosity of the binary mixture.

Isentropic compressibility ( $K_S$ ), deviation in isentropic compressibility ( $\Delta K_S$ ), intermolecular free length ( $L_f$ ), internal pressure ( $\pi_i$ ) and free volume ( $V_f$ ) are calculated using the following equations:

$$K_S = [1/(U^2\rho)] \quad (3)$$

$$\Delta K_S = (K_S)_{12} - [x_1(K_S)_1 + x_2(K_S)_2] \quad (4)$$

$$L_f = K \cdot (K_S)^{1/2} \quad (5)$$

$$\pi_i = bRT(K\eta/U)^{1/2} (\rho^{2/3} / M_{eff}^{7/6}) \quad (6)$$

$$V_f = (M_{eff}U/\eta K)^{3/2} \quad (7)$$

In Equations 5-7,  $K$  denotes the temperature-dependent Jacobson's constant and  $b$  stands for the cubic packing fraction taken as 2 for all the liquids, while  $R$  represents the universal gas constant and  $T$  refers to the experimental temperature.  $M_{eff} = \sum x_i m_i$ , where  $x_i$  denotes the mole fraction and  $m_i$  stands for the molecular weight of the  $i^{\text{th}}$  component. These calculated properties are also available at the editorial office.

Furthermore, the excess or deviation properties ( $Y$ ) recorded were fitted to the following Redlich-Kister polynomial equation by the method of least squares to derive the binary coefficients:

$$\Delta Y = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (8)$$

where  $\Delta Y$  represents the relevant excess or deviation property. The standard deviations of  $V_m^E$ ,  $\Delta\eta$ ,  $\Delta K_S$ , excess free volume ( $V_f^E$ ), excess intermolecular free length ( $L_f^E$ ) and excess internal pressure ( $\pi_i^E$ ) were calculated using the following equation:

$$\sigma(Y) = \left[ \frac{\sum (Y_{exp} - Y_{cal})^2}{(N - n)} \right]^{1/2} \quad (9)$$

where  $N$  denotes the number of data points,  $n$  represents the number of coefficients, while  $Y_{exp}$  and  $Y_{cal}$  denote experimentally obtained and theoretically calculated excess or deviation properties, respectively. The calculated values of the polynomial coefficients  $A_0$ ,  $A_1$  and  $A_2$  along with their standard deviations  $\sigma$  are given in Table 2, moreover, the results of the excess or deviation properties calculated by Equation 8 are graphically represented in Figures 1-6.

As shown in Figure 1, the  $V_m^E$  values for the binary mixtures of DEO with BVE, DEO with DIPE and DEO with AS are negative, whereas for DEO with DBE it is positive over the entire range of composition at all the studied temperatures. Furthermore, the  $V_m^E$  values decrease as the temperature increases for the mixtures of DEO with BVE, DIPE and DBE, while for DEO with AS, these  $V_m^E$  values increase as the temperature increases, indicative of the effect of the temperature. The  $V_m^E$  values are found to be more negative for DIPE with minima in the isotherm at  $x_1 = 0.5018$ , while for DBE, the  $V_m^E$  values are positive and the maximum for the excess volume observed at  $x_1 = 0.5018$ . These  $V_m^E$  values can be ordered as follows:

$$\text{DBE} > \text{AS} > \text{BVE} > \text{DIPE}$$

The negative  $V_m^E$  may be due to the interstitial accommodation of the ester molecules with an associated structure, the formation of weak molecular complexes through hydrogen bonds,  $\pi$ - $\pi$  interactions and dipole-dipole interactions. While positive  $V_m^E$  values may be

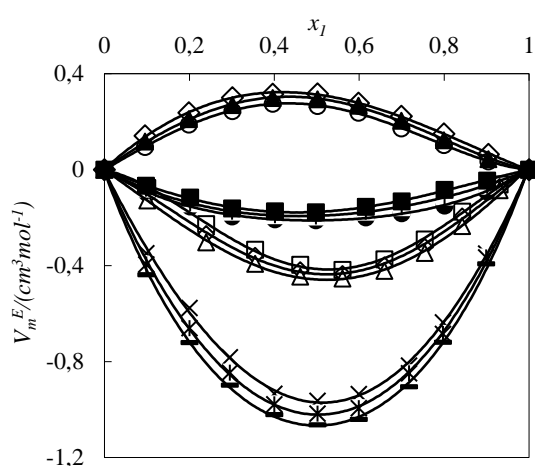


Figure 1:  $V_m^E$  vs.  $x_1$  for the binary mixtures of:

DEO with BVE at  $\square$  303.15,  $\diamond$  308.15 and  $\Delta$  313.15 K;  
 DEO with DIPE at  $\times$  303.15,  $\kappa$  308.15 and  $\text{—}$  313.15 K;  
 DEO with AS at  $\bullet$  303.15,  $+$  308.15 and  $\blacksquare$  313.15 K;  
 DEO with DBE at  $\diamond$  303.15,  $\blacktriangle$  308.15 and  $\circ$  313.15 K

attributed to the breaking of the molecular association of the components. In our present study, the molar masses of DEO, BVE, DIPE, AS and DBE are 146.14, 100.16, 102.18, 108.14 and 130.23 g·mol<sup>-1</sup>, respectively. The molar volumes of DEO at  $T = 303.15, 308.15$  and  $313.15$  K are 137.04, 137.79 and 138.52 cm<sup>3</sup>·mol<sup>-1</sup>, respectively. Furthermore, the molar volumes for the studied ethers - namely BVE, DIPE, AS and DBE - are (130.25, 131.12, 132.00), (143.28, 144.34, 145.45), (109.85, 110.37, 110.91) and (170.45, 172.44, 173.45) cm<sup>3</sup>·mol<sup>-1</sup>, respectively. These molar volumes of DEO differ slightly to those of BVE, DIPE and AS, indicating that the molecules of DEO are interstitially accommodated into clusters of BVE, DIPE and AS leading to negative  $V_m^E$  values. The increase in  $V_m^E$  values for AS as the temperature increases may confirm the presence of stronger dispersion forces or dipole-dipole interactions between the component molecules leading to greater contraction in volumes as the temperature rises. The positive  $V_m^E$  values observed for DEO and DBE may indicate weak molecular interactions.

The variation in the deviation in viscosity ( $\Delta\eta$ ) as a function of the mole fraction ( $x_1$ ) of DEO at the studied temperatures is shown in Figure 2. It was observed that for all the systems of DEO,  $\Delta\eta$  was found to be negative throughout and at the studied temperatures. These negative  $\Delta\eta$  values suggest the presence of weak dipolar forces in mixtures of liquids. It is found that  $\Delta\eta$  is large and negative for the mixtures of DEO with DIPE but less negative for the DEO with AS ones. As suggested by Hasan et al. [19], the destruction of the short-range orientation structural order in pure liquids as a result of hydrogen bonds and dipolar interactions causes dispersive interactions between unlike molecules giving rise to negative deviations in viscosity of liquid mixtures. A graphical comparison of the values of the density, viscosity and excess volume at  $T = 303.15$  and  $308.15$  K of the DEO with AS system recorded by Baragi et al. [8]

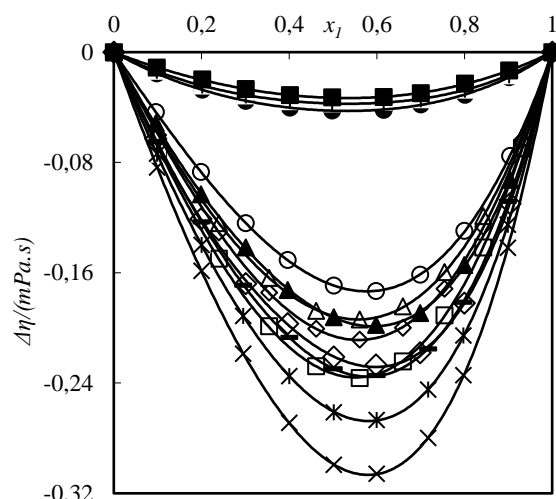


Figure 2:  $\Delta\eta$  vs.  $x_1$  for the binary mixtures of:

DEO with BVE at  $\square$  303.15,  $\diamond$  308.15 and  $\Delta$  313.15 K;  
 DEO with DIPE at  $\times$  303.15,  $\kappa$  308.15 and  $\text{—}$  313.15 K;  
 DEO with AS at  $\bullet$  303.15,  $+$  308.15 and  $\blacksquare$  313.15 K;  
 DEO with DBE at  $\diamond$  303.15,  $\blacktriangle$  308.15 and  $\circ$  313.15 K

is presented in *Figures 7-9*, respectively.

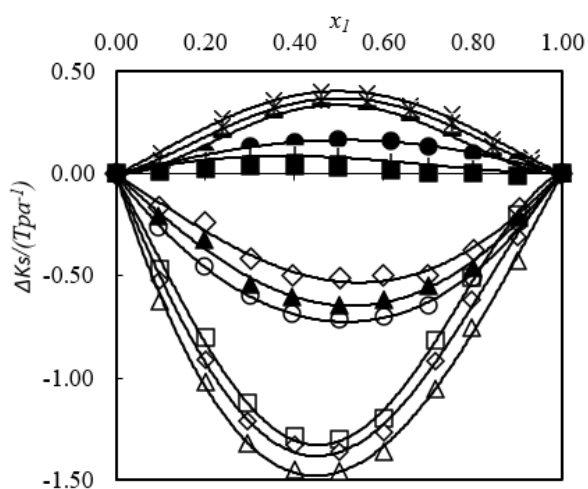


Figure 3:  $\Delta K_S$  vs.  $x_1$  for the binary mixtures of:

DEO with BVE at  $\times$  303.15,  $\text{ж}$  308.15 and  $\text{—}$  313.15 K;  
 DEO with DIPE at  $\square$  303.15,  $\diamond$  308.15 and  $\Delta$  313.15 K;  
 DEO with AS at  $\bullet$  303.15,  $+$  308.15 and  $\blacksquare$  313.15 K;  
 DEO with DBE at  $\diamond$  303.15,  $\blacktriangle$  308.15,  $\circ$  313.15 K

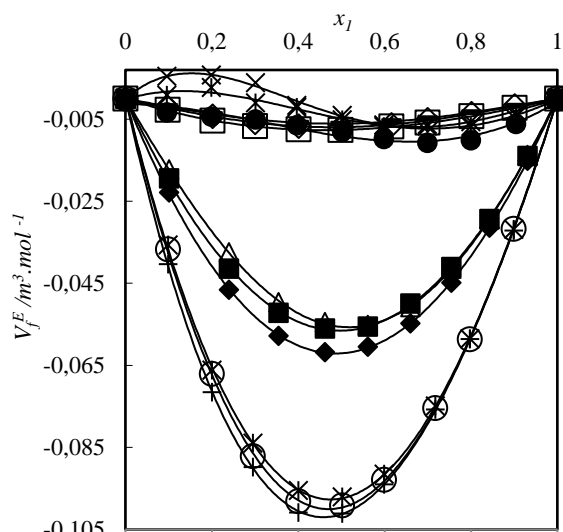


Figure 4:  $V_f^E$  vs.  $x_1$  for the binary mixtures of:

DEO with BVE at  $\blacklozenge$  303.15,  $\blacksquare$  308.15 and  $\Delta$  313.15 K;  
 DEO with DIPE at  $\text{ж}$  303.15,  $\circ$  308.15 and  $+$  313.15 K;  
 DEO with AS at  $\text{—}$  303.15,  $\diamond$  308.15 and  $\square$  313.15 K;  
 DEO with DBE at  $\times$  303.15,  $\text{ж}$  308.15 and  $\bullet$  313.15 K

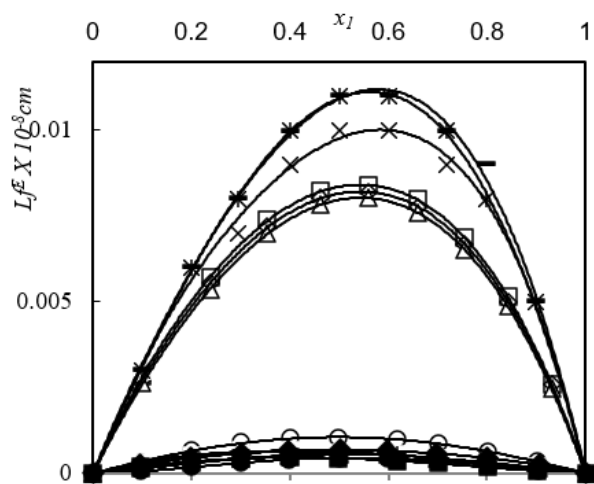


Figure 5:  $L_f^E$  vs.  $x_1$  for the binary mixtures of:

DEO with BVE at  $\square$  303.15,  $\diamond$  308.15 and  $\Delta$  313.15 K;  
 DEO with DIPE at  $\times$  303.15,  $\text{ж}$  308.15 and  $\text{—}$  313.15 K;  
 DEO with AS at  $\circ$  303.15,  $+$  308.15 and  $\blacksquare$  313.15 K;  
 DEO with DBE at  $\blacklozenge$  303.15,  $\blacktriangle$  308.15,  $\bullet$  313.15 K

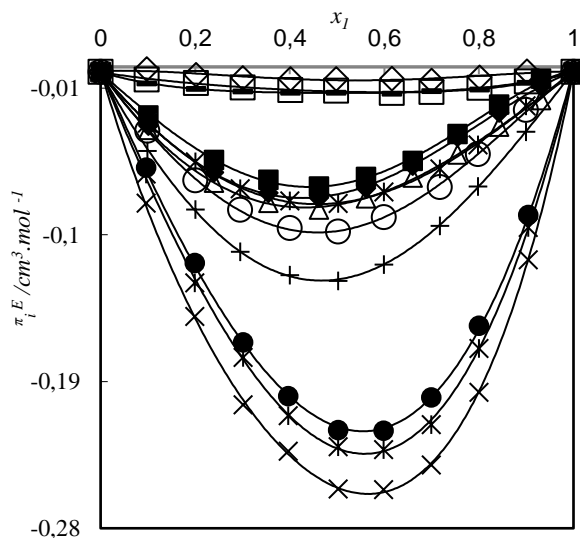


Figure 6:  $\pi_i^E$  vs.  $x_1$  for the binary mixtures of:

DEO with BVE at  $\blacklozenge$  303.15,  $\blacksquare$  308.15 and  $\Delta$  313.15 K;  
 DEO with DIPE at  $\text{ж}$  303.15,  $\circ$  308.15 and  $+$  313.15 K;  
 DEO with AS at  $\text{—}$  303.15,  $\diamond$  308.15 and  $\square$  313.15 K;  
 DEO with DBE at  $\times$  303.15,  $\text{ж}$  308.15 and  $\bullet$  313.15 K

Table 2: Parameters of Equation 8 for various functions and the corresponding standard deviations ( $\sigma$ ) of the binary mixtures at 303.15, 308.15 and 313.15 K

Binary mixture	T (K)	Excess property	$A_0$	$A_1$	$A_2$	$\sigma$
DEO + BVE	303.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-1.6578	-0.2804	1.0443	0.008
		$\Delta\eta$ (mPa·s)	-0.9331	-0.2035	0.0142	0.001
		$\Delta Ks$ (TPa <sup>-1</sup> )	1.7257	0.0902	0.6977	0.002
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.2483	0.01275	0.0028	0.000
		$L_f^E \times 10^{-8}$ (cm)	0.0335	0.0056	0.0029	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.3006	0.1191	0.0761	0.001
	308.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-1.7406	-0.2060	0.7103	0.013
		$\Delta\eta$ (mPa·s)	-0.8227	-0.2035	-0.0003	0.001
		$\Delta Ks$ (TPa <sup>-1</sup> )	1.6081	0.1759	0.4717	0.005
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.2268	0.0014	0.0173	0.001
		$L_f^E \times 10^{-8}$ (cm)	0.0322	0.0053	0.0090	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.2768	0.0957	0.1158	0.002
	313.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-1.8354	-0.1895	0.4415	0.012
		$\Delta\eta$ (mPa·s)	-0.7656	-0.1767	-0.0294	0.001
		$\Delta Ks$ (TPa <sup>-1</sup> )	1.4733	0.2236	0.3123	0.006
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.2223	-0.0150	0.0275	0.000
		$L_f^E \times 10^{-8}$ (cm)	0.0321	0.0050	-0.0004	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.3246	0.0949	0.0019	0.001
DEO + DIPE	303.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-3.8814	-0.1995	0.1160	0.016
		$\Delta\eta$ (mPa·s)	-1.1946	-0.3873	-0.0850	0.000
		$\Delta Ks$ (TPa <sup>-1</sup> )	-6.4274	0.9665	0.1169	0.013
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.3899	0.03931	0.0134	0.001
		$L_f^E \times 10^{-8}$ (cm)	0.04034	0.0121	0.0028	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.5095	0.0779	0.0665	0.001
	308.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-4.0847	-0.0394	-0.2515	0.014
		$\Delta\eta$ (mPa·s)	-1.0418	-0.3387	-0.0976	0.000
		$\Delta Ks$ (TPa <sup>-1</sup> )	-7.0499	1.2347	-0.2205	0.012
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.3978	0.0481	0.0185	0.001
		$L_f^E \times 10^{-8}$ (cm)	0.04374	0.0117	0.0003	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.3914	0.0831	0.0838	0.001
	313.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-4.2667	0.0259	-0.5911	0.018
		$\Delta\eta$ (mPa·s)	-0.9175	-0.2913	-0.0746	0.001
		$\Delta Ks$ (TPa <sup>-1</sup> )	-7.7585	1.4416	-0.5426	0.017
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.4054	0.0682	0.0011	0.000
		$L_f^E \times 10^{-8}$ (cm)	0.04370	0.0136	0.0039	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.3220	0.0624	0.0375	0.001
DEO + AS	303.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.8468	0.0252	-0.2574	0.004
		$\Delta\eta$ (mPa·s)	-0.1699	-0.0186	-0.0318	0.000
		$\Delta Ks$ (TPa <sup>-1</sup> )	0.7685	0.0434	-0.0821	0.003
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.0244	0.0016	0.0064	0.000
		$L_f^E \times 10^{-8}$ (cm)	0.0042	-0.0002	-0.0007	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.0244	0.0016	0.0064	0.000
	308.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.7708	0.1124	-0.0633	0.002
		$\Delta\eta$ (mPa·s)	-0.1491	-0.0181	-0.0306	0.000
		$\Delta Ks$ (TPa <sup>-1</sup> )	0.3415	-0.2199	0.0768	0.005
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.0277	0.0026	0.0082	0.000
		$L_f^E \times 10^{-8}$ (cm)	0.0041	-0.0037	-0.0052	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.0277	0.0026	0.0082	0.000
	313.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.7053	0.1648	0.1500	0.004
		$\Delta\eta$ (mPa·s)	-0.1336	-0.0183	-0.0041	0.000
		$\Delta Ks$ (TPa <sup>-1</sup> )	0.1518	-0.1619	-0.1085	0.002
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.0304	0.0049	0.0016	0.000
		$L_f^E \times 10^{-8}$ (cm)	0.0018	-0.0006	-0.0003	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.0489	-0.0134	-0.0172	0.001

Table 2 (continued): Parameters of Equation 8 for various functions and the corresponding standard deviations ( $\sigma$ ) of the binary mixtures at 303.15, 308.15 and 313.15 K

Binary mixture	T (K)	Excess property	$A_0$	$A_1$	$A_2$	$\sigma$
DEO + DBE	303.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	1.2523	-0.4768	-0.1035	0.005
		$\Delta\eta$ (mPa·s)	-0.8823	-0.3128	-0.1872	0.002
		$\Delta K_S$ (TPa <sup>-1</sup> )	-4.5150	-0.0774	0.1275	0.005
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.0167	-0.0595	0.0480	0.001
		$L_f^E \times 10^{-8}$ (cm)	0.0027	0.0001	0.0003	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-1.0201	-0.2342	-0.1808	0.001
	308.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	1.1863	-0.4387	-0.3837	0.005
		$\Delta\eta$ (mPa·s)	-0.7694	-0.2750	-0.1056	0.001
		$\Delta K_S$ (TPa <sup>-1</sup> )	-4.7739	-0.0111	-0.2990	0.002
		$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.0196	-0.0437	0.0106	0.001
		$L_f^E \times 10^{-8}$ (cm)	0.0035	-0.0001	-0.0095	0.000
		$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.9246	-0.2237	-0.0097	0.001
313.15	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	1.0757	-0.4354	-0.4843	0.002	
	$\Delta\eta$ (mPa·s)	-0.6759	-0.2224	-0.0089	0.000	
	$\Delta K_S$ (TPa <sup>-1</sup> )	-4.9529	0.0234	-0.2893	0.003	
	$V_f^E \times 10^{-6}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	-0.0324	-0.0315	-0.0314	0.001	
	$L_f^E \times 10^{-8}$ (cm)	0.0017	0.0004	-0.0005	0.000	
	$\pi_i^E \times 10^{-6}$ (Nm <sup>-2</sup> )	-0.8775	-0.2027	0.0535	0.001	

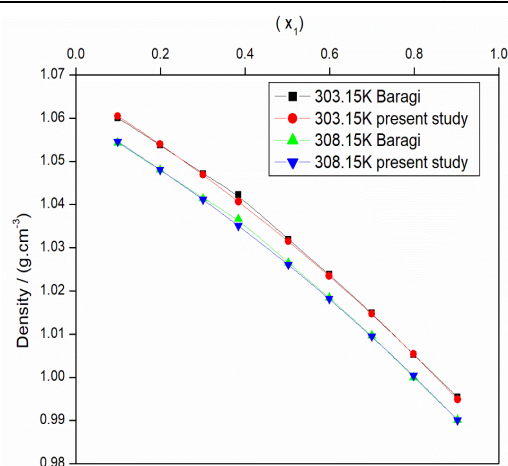


Figure 7: Comparison between the densities ( $\rho$ ) for the binary mixtures of:

AS with DEO at ■ 303.15 and ▲ 308.15 K (values measured by Baragi et al. [8])  
 DEO with AS at ● 303.15 and ▼ 308.15 K (present study)

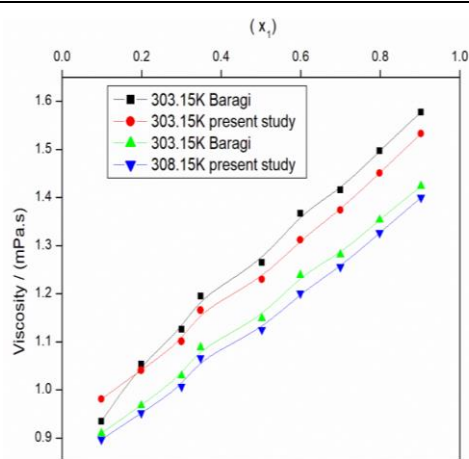


Figure 8: Comparison between the viscosities ( $\eta$ ) for the binary mixtures of:

AS with DEO at ■ 303.15 and ▲ 308.15 K (values measured by Baragi et al. [8])  
 DEO with AS at ● 303.15 and ▼ 308.15 K (present study)

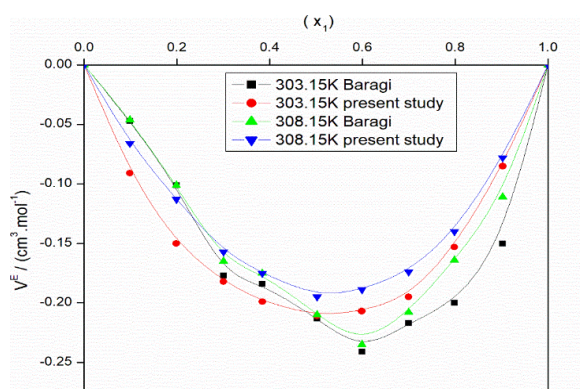


Figure 9: Comparison between the excess molar volumes ( $V_m^E$ ) for the binary mixtures of:

AS with DEO at ■ 303.15 and ▲ 308.15 K (values measured by Baragi et al. [8])  
 DEO with AS at ● 303.15 and ▼ 308.15 K (present study)

Close observation of these figures reveals that these values agree with each other quite satisfactorily. The variation in  $\Delta K_S$  with regard to the composition of the mixtures ( $x_1$  of DEO) at 303.15, 308.15 and 313.15 K is presented in [Figure 3](#). It was observed that  $\Delta K_S$  is positive for the mixtures of DEO with BVE and AS, while negative throughout for the mixtures of DEO with DIPE and DBE at all studied temperatures. Strong intermolecular interactions due to dipole-dipole interactions and interstitial accommodation result in the reduction in the deviations in the isentropic compressibility leading to negative deviations, while positive deviations indicate weak intermolecular interactions.

The variation in  $V_f^E$  for the studied DEO mixtures is plotted in [Figure 4](#). It is observed that the values of  $V_f^E$  exhibit negative deviations for the mixtures of DEO with BVE, DIPE and AS, while for the mixtures of DEO with DBE,  $V_f^E$  showed both positive and negative deviations throughout. The change from positive to negative deviations occurs at  $x_1 = 0.3965$ . This deviation in  $V_f^E$  depends on the relative strength between the contractive and expansive forces. The factors responsible for volume contraction are specific interactions between the component molecules, namely weak physical forces such as dipole-dipole or Van der Waals forces. The negative values of  $V_f^E$  suggest the existence of strong dipole-dipole interactions. Furthermore, the absolute values of  $V_f^E$  increase in the mixture of DEO with BVE as the temperature increases, suggesting the strengthening of intermolecular interactions between unlike molecules due to thermal energy. However, for the mixtures of DEO with DIPE, AS and DBE,  $V_f^E$  decreases as the temperature increases.

[Figure 5](#) shows that  $L_f^E$  is positive for all the systems. For the mixture of DEO with DIPE,  $L_f^E$  increases as the temperature increases, while for those of DEO with BVE, AS and DBE, it decreases throughout at all studied temperatures. The negative values of  $L_f^E$  show that sound waves cover long distances due to a decrease in the intermolecular free length given the strength of interactions between hydrogen bonds of unlike molecules [20]. Positive  $L_f^E$  values may be attributed to the dispersion forces [21].

The plots of the  $\pi_i^E$  against the mole fraction of DEO ( $x_1$ ) are shown in [Figure 6](#). It was observed from the plots that the values of  $\pi_i^E$  for all the systems are negative throughout, while for the mixture of DEO with DBE,  $\pi_i^E$  is more negative. The internal pressure values are a reflection of the net cohesive or adhesive forces available in the medium.

### 3.1. Estimation of the theoretical viscosity of mixtures

The theoretical viscosity of binary mixtures was calculated using the following semi-empirical relations.

Grunberg-Nissan [22] proposed the following relation:

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad (10)$$

where  $d_{12}$  denotes an interaction parameter.

Lobe [23] represented a two-parameter relation as follows:

$$V = \Phi_1 v_1 \cdot \exp(\Phi_2 \alpha_A) + \Phi_2 v_2 \cdot \exp(\Phi_1 \alpha_B) \quad (11)$$

where  $v$ ,  $v_1$  and  $v_2$  denote the kinematic viscosities of the mixtures as well as of pure liquids 1 and 2, respectively.  $\Phi_1$  and  $\Phi_2$  stand for the volume fractions of the pure components.  $\alpha_A$ , and  $\alpha_B$  represent the interaction parameters  $\alpha_A = \alpha_{AB} \ln(v_2/v_1)$  and  $\alpha_B = \alpha_{BA} \ln(v_2/v_1)$  where  $\alpha_{AB}$  and  $\alpha_{BA}$  denote parameters to fit the experimental data.

A three-parameter relation proposed by Krishnan-Laddha [24] is represented as follows:

$$\ln v = \ln v_1 + x_2 \ln v_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln[x_1 M_1 + x_2 M_2] - 2.303 x_1 x_2 [B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2] \quad (12)$$

where  $v$ ,  $v_1$  and  $v_2$  refer to kinematic viscosities, while  $B_{12}$ ,  $C_{12}$  and  $D_{12}$  are binary coefficients.

The predictive ability of [Equations 10-12](#) was tested by estimating the percentage standard deviation  $\sigma(\%)$  between the experimental and determined viscosities as follows:

$$\sigma(\%) = \left[ \frac{1}{(n-k)} \sum \{100(n_{exp} - n_{cal})/n_{exp}\}^2 \right]^{1/2} \quad (13)$$

where  $n$  represents the number of data points in each set and  $k$  denotes the number of numerical coefficients in the equation, while  $n_{exp}$  and  $n_{cal}$  denote experimentally obtained and theoretically calculated mixtures viscosities, respectively.

The values of the interaction parameters measured from the above relations together with the percentage standard deviations  $\sigma(\%)$  are reported in [Table 3](#). A close examination of the values of  $\sigma(\%)$  reveals that the  $\sigma(\%)$  values for one parameter of the Grunberg-Nissan equation fall between 0.01 and 0.05, for two of the Lobe equation between 0.00 and 0.04, while for 3 of the Krishnan-Laddha equation between 0.00 and 0.01. From these  $\sigma(\%)$  values, it can be concluded that the three parameters of the Krishnan-Laddha relation calculate the theoretical viscosity more satisfactorily than the other two models.

## 4. Conclusions

The density, viscosity and speed of sound data have been described for binary mixtures of diethyl oxalate with butyl vinyl ether, diisopropyl ether, anisole and dibutyl ether at 303.15, 308.15 and 313.15 K over the whole range of the composition. Using the experimental data, the various excess or deviation properties - namely  $V_m^E$ ,  $\Delta\eta$ ,  $\Delta K_S$ ,  $V_f^E$ ,  $L_f^E$  and  $\pi_i^E$  - were assessed. All the calculated excess or deviation properties exhibited either positive or negative deviations as a result of the effect of the temperature. These excess parameters are indicative of the weak interactions (dispersion forces) between

Table 3: Adjustable parameters and percentage standard deviations ( $\sigma\%$ ) of several correlations regarding the viscosity models tested for the viscosities of binary mixtures

Binary Mixture	T(K)	Grunberg-Nissan		Lobe			Krishnan-Laddha			
		$d_{12}$	$\sigma\%$	$\alpha_A$	$\alpha_B$	$\sigma\%$	$B_{12}$	$C_{12}$	$D_{12}$	$\sigma\%$
DEO + BVE	303.15	-0.1004	0.05	0.7045	-0.3677	0.02	0.0519	-0.0267	-0.0191	0.01
	308.15	-0.1068	0.03	0.8094	-0.4976	0.01	0.0607	-0.0203	-0.0110	0.01
	313.15	-0.1482	0.05	0.8061	-0.4579	0.01	0.0712	-0.0268	0.0020	0.01
DEO + DIPE	303.15	-0.2144	0.03	0.7878	-0.5180	0.01	0.1055	-0.0168	-0.0049	0.01
	308.15	-0.1851	0.02	0.8573	-0.6411	0.01	0.0912	-0.0096	0.0096	0.01
	313.15	-0.1477	0.01	0.9464	-0.7820	0.01	0.0762	-0.0001	0.0060	0.01
DEO + AS	303.15	0.0131	0.01	1.6888	-1.3706	0.01	-0.0148	0.0017	0.0112	0.00
	308.15	0.0178	0.01	1.6912	-1.3825	0.01	-0.0175	0.0020	0.0123	0.00
	313.15	0.0242	0.01	1.7449	-1.4375	0.00	-0.0190	0.0036	0.0017	0.00
DEO + DBE	303.15	-0.4299	0.04	0.7705	-0.3050	0.04	0.1662	0.0080	0.0431	0.01
	308.15	-0.3902	0.03	0.8762	-0.4831	0.02	0.1540	0.0173	0.0099	0.01
	313.15	-0.3412	0.04	0.6955	-0.3286	0.02	0.1384	0.0163	-0.0287	0.01

DEO and DBE, while for the other mixtures the strong interactions of charge transfer and dipole-induced dipole forces are implied. It may be suggested that molecular interactions between esters and ethers through hydrogen bonding and dipole-dipole interactions may be present.

In comparison with our earlier work [25], the present reported system of DEO with ethers was found to yield stronger molecular interactions perhaps due to the molecular weight of vinyl acetate being less than that of DEO, resulting in a reduction in the flow time observed for vinyl acetate because smaller molecules are not resistant to flow. Therefore, in the case of vinyl acetate, thinner and less viscous substances are produced.

Additionally, it can be concluded that the carbonyl oxygen of DEO may interact with the hydrogen of ethers, resulting in stronger hydrogen bonding.

### Nomenclature

$\rho$	density ( $\text{g}\cdot\text{cm}^{-3}$ )
$\Delta\eta$	deviation in viscosity ( $\text{mPa}\cdot\text{s}$ )
$\Delta K_S$	deviation in isentropic compressibility ( $\text{TPa}^{-1}$ )
$V_m^E$	excess molar volumes ( $\text{cm}^3\cdot\text{mol}^{-1}$ )
$V_f^E$	excess free volume ( $\text{m}^3\cdot\text{mol}^{-1}$ )
$L_f^E$	excess intermolecular free length (cm)
$\pi_i^E$	excess internal pressure ( $\text{Nm}^{-2}$ )
$V_f$	free volume ( $\text{m}^3\cdot\text{mol}^{-1}$ )
$K_S$	isentropic compressibility ( $\text{TPa}^{-1}$ )
$L_f$	intermolecular free length (cm)
$\pi_i$	internal pressure ( $\text{Nm}^{-2}$ )
$x_j$	mole fraction of component
$\eta$	viscosity ( $\text{mPa}\cdot\text{s}$ )
$U$	speeds of sound ( $\text{ms}^{-1}$ )

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