Volumetric and Viscometric Studies of Binary Mixtures of Diethyl Carbonate with 1,2-Dichlorobenzene at Various Temperatures

A.Venkateswara Rao[a], K. Narendra[b,*], T.S. Krishna[c], P. Bharath[a], D. Ramachandran[a,¥]

[a]*Department of Chemistry, Acharya Nagarjuna University, Guntur -10*
[b]*Department of Physics, V.R. Siddhartha Engineering College, Vijayawada - 07*
[c]*Department of Physics, P.B. Siddhartha College of Arts&Science, Vijayawada - 10*

*E-mail address: narenk75@gmail.com
¥E-mail:dittakavirc@gmail.com

Abstract

Densities, speeds of sound and viscosities have been measured at 303.15 to 318.15 K and at atmospheric pressure for binary mixtures of Diethyl carbonate (DEC) with 1,2-dichlorobenzene over the entire composition range. With the measured experimental values, the excess properties such as, excess molar volume, V_m^E*, excess isentropic compressibility,* κ_s^E*, excess molar isentropic compressibility,* $K_{s,m}^E$*, excess speed of sound,* u^E*, excess isobaric thermal expansion,* α_p^E*, deviation in viscosity,* $\Delta\eta$ *, and excess Gibbs energy of activation,* ΔG^{*E}*, of viscous flow of the investigated mixtures were calculated. This study plays a prominent role in many industries, from organic synthesis to separating ion-exchange media. Understanding excess thermodynamics and transport properties for binary mixtures are extremely important because they help us to understanding molecular structure and interactions. For better knowledge of the solute and solvent interaction, excess partial molar volumes,* $\bar{V}_{m,1}^{E}$ *and* $\bar{V}_{m,2}^{E}$*, and excess partial molar volumes,* $\bar{V}_{m,1}^{\circ E}$ *and* $\bar{V}_{m,2}^{\circ E}$ *of the components at infinite dilution have been measured. All the excess parameter values have been fitted using the R-K polynomial smoothing equation. The results have been analysed in terms of molecular interactions and structural effects. In addition, excess molar volume of the mixture has done through the Prigogine–Flory–Patterson theory.*

Keywords: *DEC, 1,2-dichlorobenzene, excess Gibb's free energy, excess parameters, excess partial molar volume, PFP theory*

1. Introduction

The volumetric characteristics of binary combinations, as well as their familiarity with composition and temperature dependency, provide significant information on the molecular influence on the strength of intermolecular interactions between component molecules [1].

In both theoretical and practical research, understanding the physicochemical characteristics of liquids and the mixes made up of these liquids is crucial. In fields like chemical, textile, leather, and nuclear industries, the results are typically employed in design procedures like flow, mass, or heat transfer calculations. In order to analyse molecular interactions and other aspects like size, shape, packing effect, etc., it is vital to consider the volumetric and acoustic properties of liquids and their mixtures. [2,3]

The investigations we conducted previously with methyl phenols [4] and diethyl carbonate (DEC) [5] are continued in the current work. An ester called DEC is largely used as a solvent in medicinal applications and as an electrolyte in batteries [6]. It shows significant potential as a fuel additive (40.6% oxygen by mass) to help in cleaner diesel combustion due to its high boiling point, which may minimize fuel volatility and result in little vapor build-up [7].

Additionally, they have industrial relevance as lubricants with the new HFCs and as gasoline additives. An intermediary for dyes and a few agricultural compounds is 1,2-dichlorobenzene [8,9].

Measured experimental density, speed of sound and viscosity values of studied blended used to calculate the excess values of molar volume, V_m, isentropic compressibility, κ_s, molar isentropic compressibility, $K_{s,m}$, speed of sound, *u*, isobaric thermal expansion, α_p, deviation in viscosity, $\Delta\eta$, excess Gibbs energy of activation, ΔG^{*E}, of viscous flow and excess partial molar volumes $\bar{V}_{m,i}^{E,\infty}$ at infinite dilution for DEC with 1,2-dichlorobenzene at 303.15 - 318.15 K over the whole mole fraction range underatmospheric pressure.

2. Materials and methods

The mass fraction purities of the liquids from Sigma-Aldrich, USA were as follows: DEC (99%) and 1,2-dichlrobenzene (99%). Prior to experimental measurements, all liquids were used after double distillation and partially degassed with a vacuum pump under inert atmosphere. The purity of these solvents was ascertained by comparing the measured density, speed of sound and viscosity of the pure components with the available literature [10-22] as shown in Table 1.

The preparations of the samples were carried out just prior to the measurements with an electronic balance (CPA-225D, Sartorius, Germany) capable of measuring precisely within $\pm 1\times10^{-5}$ *g. The mole fraction uncertainty was found to be within* $\pm 1\times10^{-4}$.

Densities measurements were carried out using a single-capillary pycnometer (Borosil- bulb capacity of ≈10mL). The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. Use was made of triple distilled water to calibrate the graduations on the pycnometer and the density values of pure water compared with that from literature with the reproducibility seen to be within ± 1 *kg* m^{-3}. *The speeds of* *sound were measured by a variable-path, single-crystal multi frequency ultrasonic interferometer (F-81, Mittal Enterprises, India) working at 2 MHz and was found to be reproducible within ± 0.8 m* s^{-1}*. Temperature measurements were carried out using a Julabo (FT 200, Julabo Labortechnik, Gmbh, Germany) thermostatic bath having an accuracy of ±0.02 K. A self-optimizing electronic PID-control circuit automatically adjusts the heat supply to the value required by the bath and pressure was kept at ambient.*

An Ostwald's viscometer was used to measure the viscosities of pure liquids and their binary mixtures. The calibration of viscometer was done with tripled distilled water at 303.15 to 318.15 K. To minimize the possibility of presence of thermal fluctuations, the viscometer containing the sample under investigation was allowed to stand for 30 minutes in a thermostatic water bath. A digital stop-watch with an accuracy of ±0.01 s was used to record the time of flow in triplicate. The temperatures of the liquids under investigation were maintained at an accuracy of ±0.02 K in an electronically controlled thermostatic water bath.

Table 1. Density, speeds of sound, and viscosity of the pure liquid components at 303.15-318.15 K, at 0.1 MPa.

Compound	T/K	ρ/kg m^{-3}		u/m s^{-1}		η/m Pa s	
		Expt.	Ref.	Expt.	Ref.	Expt.	Ref.
DEC	303.15	963.5	963.65 [12]	1156.9	1156.0 [13]	0.701	0.702[15]
			963.40 [13]		1156.3 [14]		
			963.60 [14]		1156.0 [16]		
			963.70 [15]		1156.6 [19]		
			963.58 [16]				
			963.00 [17]				
			963.60 [18]				
			963.70 [19]				
	308.15	957.8	957.90 [10]	1136.6	1135.7 [10]	0.656	0.659[15]
			957.90 [11]		1135.8 [14]		
			957.92 [14]		1136.0 [16]		
			958.00 [15]		1136.3 [19]		
			957.93 [16]				
			957.50 [17]				
			957.98 [18]				

			958.10 [19]				
	313.15	952.1	952.31 [12]	1116.5	1115.0 [13]	0.621	0.620[15]
			952.20 [13]		1116.0 [16]		
			952.40 [15]		1116.1 [19]		
			952.26 [16]				
			952.00 [17]				
			952.40 [19]				
	318.15	946.4	946.43 [10]	1096.5	1096.2 [19]	0.596	0.584[23]
			946.70 [15]				
			947.67 [18]				
			946.70 [19]				
1,2-dichlorobenzene	303.15	1294.7	1294.72[20]	1263.0	1265 [20]	1.238	1.235 [20]
			1295.4[21]		1266 [22]		1.214 [21]
			1295.45[22]				
	308.15	1289.7	1289.13[20]	1243.0	1246 [20]	1.146	1.144 [20]
			1289.7 [21]				1.105 [21]
			1289.13[22]				
	313.15	1283.8	1276.53[22]	1222.0	1237[22]	1.054	-
	318.15	1277.9	-	1203.0	-	0.974	-

Expt. – Experimental, Ref. - Reference

3. Theory

Excess Properties

The measured values density (ρ), speed of sound (u) and viscosity (η) of binary mixtures of DEC with 1,2-dichlorobenzene as mole fraction, x_1 of DEC at 303.15 to 318.15 K are listed in Table 2.

Table 2: Mole fraction of DEC (x_1), density (ρ), speed of sound (u) and viscosity (η) at 303.15 to 318.15 K for the binary mixtures of DEC with 1,2-dichlorobenzene.

x_1	ρ/kg m^{-3}	u/m s^{-1}	η/m Pa s	ρ/kg m^{-3}	u/m s^{-1}	η/m Pa s
	T = 303.15 K			T = 308.15 K		
0.0000	1294.7	1263.0	1.238	1289.7	1243.0	1.146
0.0906	1262.9	1252.3	1.184	1257.8	1233.5	1.096
0.2012	1224.6	1240.4	1.120	1219.4	1222.3	1.036
0.3243	1182.5	1227.3	1.051	1177.2	1209.5	0.973
0.4122	1152.9	1218.0	1.003	1147.5	1200.3	0.929
0.5001	1123.6	1208.7	0.955	1118.1	1190.9	0.885
0.5985	1091.2	1198.4	0.904	1085.7	1180.3	0.838
0.7013	1057.8	1187.7	0.851	1052.3	1169.2	0.790
0.8102	1022.9	1176.3	0.795	1017.4	1157.3	0.740
0.8994	994.8	1167.0	0.751	989.2	1147.4	0.700
1.0000	963.5	1156.8	0.701	957.8	1136.5	0.656
	T = 313.15 K			T = 318.15 K		
0.0000	1283.8	1222.0	1.054	1277.9	1203.0	0.974
0.0906	1251.9	1213.8	1.008	1246.0	1195.5	0.932
0.2012	1213.5	1203.3	0.955	1207.6	1185.3	0.884
0.3243	1171.4	1191.1	0.898	1165.5	1173.3	0.834
0.4122	1141.7	1182.0	0.859	1135.8	1164.2	0.800
0.5001	1112.3	1172.6	0.821	1106.5	1154.8	0.767
0.5985	1079.9	1161.9	0.779	1074.1	1144.0	0.731
0.7013	1046.5	1150.5	0.736	1040.7	1132.3	0.694
0.8102	1011.7	1138.2	0.693	1005.9	1119.6	0.656
0.8994	983.5	1128.1	0.659	977.8	1108.9	0.627
1.0000	952.1	1116.4	0.621	946.4	1096.4	0.596

The following equation was used to get the molar volume:

$$V_m = \frac{x_1 M_1 + (1-x_1) M_2}{\rho} \tag{1}$$

To obtain excess molar volume data, the following equation was used from the densities of pure liquids and their mixtures:

$$V_m^E = V_m - V_m^{id} = \frac{x_1 M_1 + (1-x_1) M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{(1-x_1) M_2}{\rho_2}\right) \tag{2}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are molar masses, and ρ_1 and ρ_2 are the densities of the pure liquid components 1 and 2, respectively.

The isentropic compressibility coefficients, κ_S, derived directly from the speed of sound and density measurements using the Newton-Laplace equation [23]:

$$\kappa_s = (\rho u^2)^{-1} \qquad (3)$$

Molar isentropic compressibility can be calculated by the following relation

$$K_{s,m} = \kappa_s V_m \qquad (4)$$

Excess isentropic compressibility and excess molar isentropic compressibility can be determined using the relations, [24]

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \qquad (5)$$

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{id} \qquad (6)$$

where κ_S is isentropic compression, κ_s^{id} is isentropic compression of the ideal mixture, and $K_{s,m}^{id}$ is the molar isentropic compressibility of the ideal mixture. κ_s^{id}, $K_{s,m}^{id}$ values for binary mixtures were computed according to Benson and Kiyohara [25] recommendations

$$\kappa_{\mathrm{s}}^{\mathrm{id}} = \sum_{\mathrm{i}=1}^{2} \varphi_{\mathrm{i}} \left[\kappa_{\mathrm{s.i}} + TV_{\mathrm{i}} \left(\alpha_{\mathrm{i}}^{2} \right) / C_{\mathrm{p.i}} \right] - \left\{ T \left(\sum_{\mathrm{i}=1}^{2} x_{\mathrm{i}} V_{\mathrm{i}} \right) \left(\sum_{\mathrm{i}=1}^{2} \varphi_{\mathrm{i}} \alpha_{\mathrm{i}} \right)^{2} / \sum_{\mathrm{i}=1}^{2} x_{\mathrm{i}} C_{\mathrm{p.i}} \right\} \qquad (7)$$

$$K_{S,m}^{id} = x_1 K_{s,\mathrm{m},1} + x_2 K_{s,m,2} + T \left[\frac{x_1 \left(V_{m,1} \alpha_{p,1} \right)^2}{C_{p,1}} + \frac{x_2 \left(V_{m,2} \alpha_{p,2} \right)^2}{C_{p,2}} - \frac{\left(V_m^{id} \alpha_p^{id} \right)^2}{C_p^{id}} \right] \qquad (8)$$

V_m^{id} , α_p^{id} and C_p^{id} are calculated using the following relations given in our previous paper [5]:

The values of α_{p} are calculated from the temperature dependence of the density data of pure liquids and linear with temperature by using the relation,

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \qquad (9)$$

The expected uncertainty of α_p is within ±0.003kK^{-1}.

The excess speed of sound, u^E, was calculated using the relation

$$u^E = u - u^{id} \qquad (10)$$

The speed of sound in an ideal mixture can be determined by the equation

$$u^{id} = \left(\frac{V_m^{id}}{\kappa_s^{id} M} \right)^{1/2} \qquad (11)$$

Excess isobaric thermal expansivity

Since the electrolytes are known as the “blood” of the batteries, the volume expansion property of mixture solvents is helping understand the stability of electrolyte systems in their application, especially in higher temperatures. Isobaric thermal expansions are estimated for every composition in order to gain a better understanding of the structural change that occurs during mixing.

α_p^E which have been often used the following equation:

$$\alpha_p^E / (K^{-1}) = \alpha_p - \alpha_p^{id} = (\partial V_m / \partial T)_p / V_m - \sum_{i=1}^{2} \phi_i \alpha_{p,i}^{*} \qquad (12)$$

where, V_m is the molar volume of the mixture, ϕ_i is the volume fraction of component ‘i’ in the pre-mixing state, and α_i^* is the thermal expansion coefficient of the pure component ‘i’.

The viscosity deviation from a linear dependence on mole fraction were calculated from

$$\Delta\eta = \eta_{mix} - (x_1\eta_1 + x_2\eta_2) \qquad - \qquad (13)$$

where x and η are the mole fraction and viscosities, subscripts 1 and 2 represents the 1st and 2nd components respectively. η_{mix} is the viscosity of the mixture.

$$\Delta G^{*} = RT\,ln\left(\frac{\eta V}{hN_A}\right) \qquad (14)$$

$$\Delta G^{*E} = RT\left[ln\left(\frac{\eta V}{\eta_2 V_2}\right) - x_1\,ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right)\right] \qquad (15)$$

where V,V_1 and V_2 are the molar volumes of the binary mixture DEC and 1,2-dichlorobenzene in $m^3.mol^{-1}$ respectively, η, η_1 and η_2 are the viscosities of binary mixture respectively. x_1 is the mole fraction of DEC and h, N_A and R are Planck's constant, Avogadro's number and gas constant respectively.

The Redlich-Kister [26] polynomial equation was used to fit the excess values of the above parameters for the mixtures.

$$Y^{E} = x_1 x_2 \sum_{i=0}^{j} A_i \left(2x_1 - 1\right)^i \qquad (16)$$

where Y^E is V_m^E, κ_s^E, $K_{s,m}^E$, u^E, and α_p^E. The equation coefficients, A_i, obtained by the method of least squares with equal weights assigned to each point were calculated along with the standard deviation $\sigma(Y^E)$. The coefficients were adjustable parameters for a better fit of the excess functions.

The standard deviation $\sigma(Y^E)$ is calculated using,

$$\sigma(Y^E) = \left(\frac{\sum\left(Y^E_{expt} - Y^E_{cal}\right)^2}{(m-n)}\right)^{1/2} \qquad (17)$$

where m equal to the number of experimental points, n is the number of A_i coefficients considered (j + 1 in the present study). The optimal number of A_i coefficients has been determined statistically by performing F-test. The coefficients, A_i and corresponding standard deviations, σ fit of V_m^E , κ_s^E $K_{s,m}^E$, u^E, α_p^E, ΔG^{*E} standard error (σ), and standard deviation was given in Table 3. The variations of V_m^E, κ_s^E, $K_{s,m}^E$, u^E, α_p^E, $\Delta\eta$ and ΔG^{*E} with mole fraction, x_1 along with smoothed values from Eq. (16) at studied temperatures are shown graphically in Figures 1-7 respectively.

Table 3. Coefficients A_j of equation (16) along with standard deviations σ of binary mixture properties.

Parameter	T/K	A_0	A_1	σ
$V_m^E/10^6$ $m^3\,mol^{-1}$	303.15	-0.3567	0.0569	0.0011
	308.15	-0.4021	0.0558	0.0009
	313.15	-0.4489	0.0459	0.0018
	318.15	-0.4972	0.0288	0.0035
$\kappa_s^E/10^{10}$	303.15	-1.1457	-0.0939	0.0014
	308.15	-1.2720	-0.1016	0.0007

m^2 N^{-1}	313.15	-1.4137	-0.1150	0.0007
	318.15	-1.5732	-0.1530	0.0020
$K_{\mathrm{s,m}}^{\mathrm{E}}/10^{14}$ m^5 N^{-1} mol^{-1}	303.15	-1.3751	-0.1642	0.0015
	308.15	-1.5354	-0.1826	0.0007
	313.15	-1.7166	-0.2092	0.0011
	318.15	-1.9217	-0.2677	0.0029
u$^{\mathrm{E}}$/10^2 m s^{-1}	303.15	1.0862	-0.2062	0.0007
	308.15	1.1441	-0.2263	0.0010
	313.15	1.2034	-0.2421	0.0020
	318.15	1.2675	-0.2427	0.0029
$\alpha_p^E/10^3$ K^{-1}	303.15	-3.0175	-0.3667	0.0006
	308.15	-3.3865	-0.3363	0.0006
	313.15	-3.7609	-0.2331	0.0006
	318.15	-4.1438	-0.0713	0.0003
Δη / m Pa s	303.15	-5.56E^{-02}	9.31E^{-03}	1.43E^{-04}
	308.15	-6.23E^{-02}	8.88E^{-03}	7.64E^{-05}
	313.15	-0.0693	0.0092	0.0004
	318.15	-0.0755	0.0090	0.0007
ΔG$^{*\mathrm{E}}$ / J mol^{-1}	303.15	257.8225	60.6827	0.6309
	308.15	215.9473	50.4154	0.1130
	313.15	142.1270	34.6676	0.8489
	318.15	56.6679	16.6848	2.3374

Partial molar properties

The partial molar quantities determine the variations in molecular configuration of the non-ideal components system. The partial molar properties $\bar{Y}_{m,1}$ and $\bar{Y}_{m,2}$ of DEC and 1,2-dichlorobenzene of whole mole fraction range were investigated using the following relations:

$$\bar{Y}_{m,1} = Y_s^E + Y_{m,1}^* + x_2\left(\frac{\partial Y_s^E}{\partial x_1}\right)_{T,p} \qquad (18)$$

$$\bar{Y}_{m,2} = Y_s^E + Y_{m,2}^* - x_1\left(\frac{\partial Y_s^E}{\partial x_1}\right)_{T,p} \qquad (19)$$

where Y is V or K_s where $Y_{m,1}^*$ and $Y_{m,2}^*$ are the molar properties of pure DEC and 1,2-dichlorobenzene. The derivative $(\partial Y_s^E / \partial x_1)_{T,p}$ in Eq. (17) and (18) could be measured by differentiation of R.K, and leads to the equations for $\bar{Y}_{m,1}$ & $\bar{Y}_{m,2}$.

$$\bar{Y}_{m,1} = \bar{Y}_{m,1}^* + x_2^2\sum_{i=0}^{j} A_i(2x_1-1)^i - 2x_1x_2^2\sum_{i=0}^{j} A_i(2x_1-1)^{i-1} \qquad (20)$$

$$\overline{Y}_{m,2} = \overline{Y}^{*}_{m,2} + x_1^2 \sum_{i=0}^{j} A_i (2x_1 - 1)^i + 2x_2 x_1^2 \sum_{i=0}^{j} A_i (2x_1 - 1)^{i-1} \quad (21)$$

The excess partial molar properties were calculated by following relations:

$$\overline{Y}^{E}_{m,i} = Y^E_m + (1 - x_1)(\partial Y^E_m / \partial x_i) \quad (22)$$

To calculate the partial molar properties of DEC at infinite dilution(x$_1$=0) in 1,2-dichlorobenzene, and the partial molar properties of 1,2-dichlorobenzene at infinite dilution(x$_2$=0) in DEC. Therefore, $\overline{Y}^{\circ}_{m,1}$ can be calculated by setting x_1=0 which leads to

$$\overline{Y}^{\circ}_{m,1} = Y^{*}_{m,1} + \sum_{i=0}^{n} A_i (-1)^i \quad (23)$$

Similarly setting x_2=0, leads to

$$\overline{Y}^{\circ}_{m,2} = Y^{*}_{m,2} + \sum_{i=0}^{n} A_i \quad (24)$$

where $\overline{Y}^{\circ}_{m,1}$ and $\overline{Y}^{\circ}_{m,2}$ represent the partial molar properties of DEC at infinite dilution in 1,2-dichlorobenzene and the partial molar properties of 1,2-dichlorobenzene at infinite dilution in DEC, respectively.

Excess partial molar properties at infinite dilution $\overline{Y}^{\circ,E}_{m,i}$ for each component in binary liquid mixtures were evaluated through relations

$$\overline{Y}^{\circ,E}_{m,1} = \overline{Y}^{\circ}_{m,1} - Y^{*}_{m,1} \quad (25)$$

$$\overline{Y}^{\circ,E}_{m,2} = \overline{Y}^{\circ}_{m,2} - Y^{*}_{m,2} \quad (26)$$

4. Discussion

Figure 1 depicts the variation of excess molar volume with mole fraction of DEC at various temperatures. The excess volume is controlled by (i) the loss of dipolar interaction in DEC when 1,2-dichlorobenzene is added. (ii) Dipole-dipole and donor-acceptor interactions between dissimilar molecules, and (iii) the fitting of smaller molecules into holes caused by larger molecules. The first impact causes volume to expand, resulting in positive numbers, while the following two causes volume to contract, resulting in negative values. The real values are determined by the sum of these conflicting contributions. The investigation's experimental results indicate that the component responsible for volume expansion is prominent over the full composition range in binary mixes.

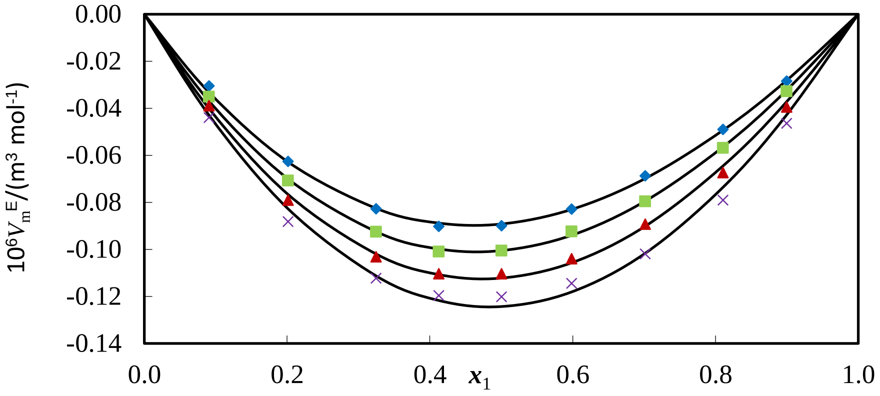

Fig 1. Plots of excess molar volume, V_m^E *vs.* mole fraction, x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and lines represent values calculated from R-K equation using the coefficients given in Table 3.

Figs.2 and 4 shows the behavior and dependence of excess isentropic compressibility, κ_s^E and excess speed of sound, u^E with mole fraction, x_1 of DEC with 1,2-dichlorobenzene over the entire composition range at different temperatures. The κ_s^E values are observed to be negative and become more negative with increase of temperature. From Fig.4, u^E values are observed to positive and become more positive with increase in temperature. This acoustic parameter provides information about the molecules' interactions with each other within a suspension. According to current literature, as the population of molecules increases, their intermolecular interactions increase, causing them to build interactions with their neighbors, which causes the solution to become more compact and resistant to movement. Thus, the u^E value increases, which results in positive values. It is owing to the presence of a strong specific contact between DEC and 1,2-dichlorobenzene, as well as the fitting of smaller DEC molecules into the gaps left by bigger 1,2-dichlorobenzene molecules.

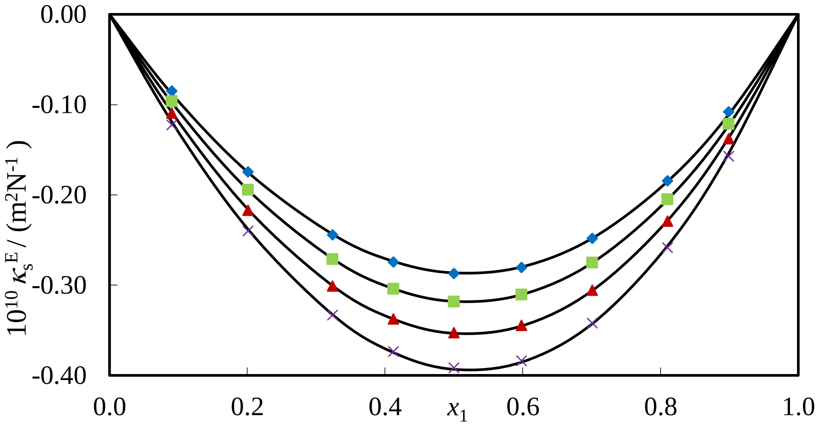

Fig 2.Variation of excess isentropic compressibility, κ_s^E *vs.* mole fraction x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and solid lines have been drawn from R-K equation using the coefficients given in Table 3.

The values can be interpreted in terms of two opposing effects: I loss of mutual dipolar association and difference in size and shape of dissimilar molecules, and (ii) dipole–induced dipole, dipole–dipole, electron-donor–acceptor interactions, and interstitial accommodation of the non-common component in the carbonate lattice. As indicated by Jacobson [27], the first effect adds to an increase in free length. This results in a negative departure in sound speed and a positive deviation in isentropic excess compressibility. In contrast, the latter effect results in a positive departure in sound speed and a negative deviation in excess isentropic compressibility. The sign and size of the actual deviation are determined by the respective magnitudes of the two opposing effects [28]. Examining the curves in Figs. 2 and 4 indicates that the latter effect predominated in all binary mixes.

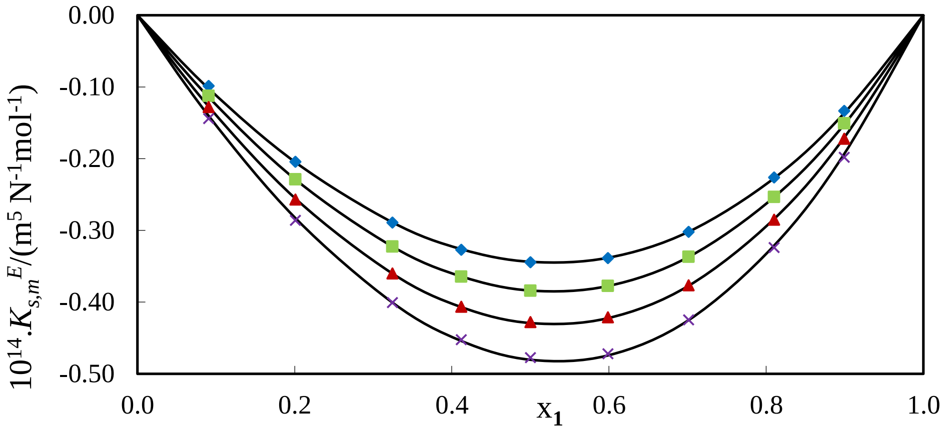

Fig.3. Excess molar isentropic compressibility ($K_{s,m}^{E}$) with mole fraction x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and solid lines have been drawn from R-K equation using the coefficients given in Table 3.

Figure 3 depicts the variations of $K_{s,m}^{E}$, that occur in the case of 1,2-dichlorobenzene with DEC concentration and temperature. The values of $K_{s,m}^{E}$ were negative for the binary system investigated, and they became more negative as the temperature increased. The rise in $K_{s,m}^{E}$ is attributable to the possibility of smaller solvent molecules being accommodated in DEC free volumes, and particular interactions within binary mixes reinforce the negative behaviour of $K_{s,m}^{E}$

Isobaric thermal expansion α_{p}^{E} values were determined for each composition to better understand the change in the structure of the solution after mixing. Figure 5 depicts the excess isobaric thermal expansivity α_{p}^{E} values measured at 303.15 - 318.15 K for the binary mixes. At all temperatures, negative values α_{p}^{E} of were recorded. Negative results for the examined combination imply significant dipole-dipole interactions between DEC and 1,2-dichlorobenzene, as well as more closed packing of the constituents of the mixes in mixed state vs pure state.

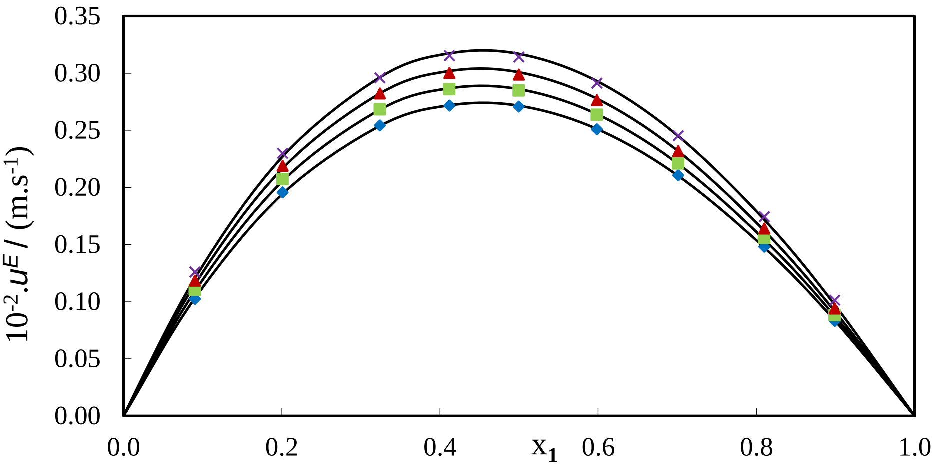

Fig.4. Excess speed of sound (u^E) with mole fraction x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and solid lines have been drawn from R-K equation using the coefficients given in Table 3.

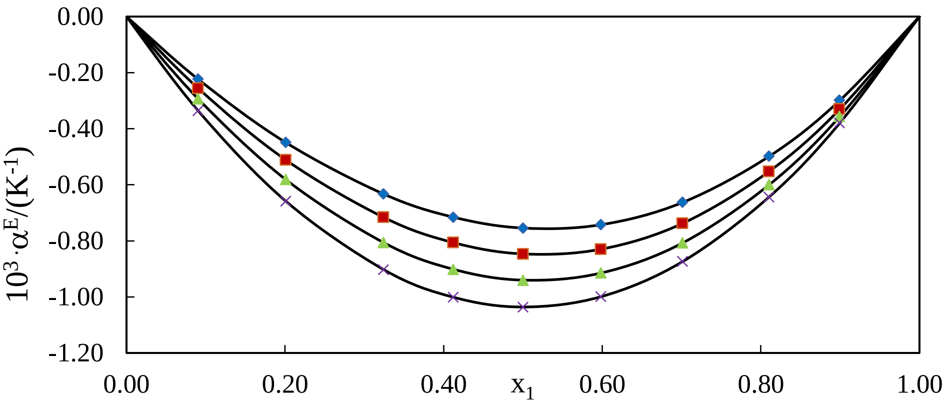

Fig.5. Excess isobaric expansivity (α^E) with mole fraction x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and solid lines have been drawn from R-K equation using the coefficients given in Table 3.

The viscosity of liquid mixtures is far from being ideal as liquids blend together. Viscosity can deviate from ideal mixture behavior because of interactions as well as size and shape [29]. The magnitude of the deviation, and whether the deviation is a positive or negative response, is influenced by temperature, the size and shape of the molecules in the mixture. From Fig.6, the systematic increase of Δη values with temperature is observed in the present study.

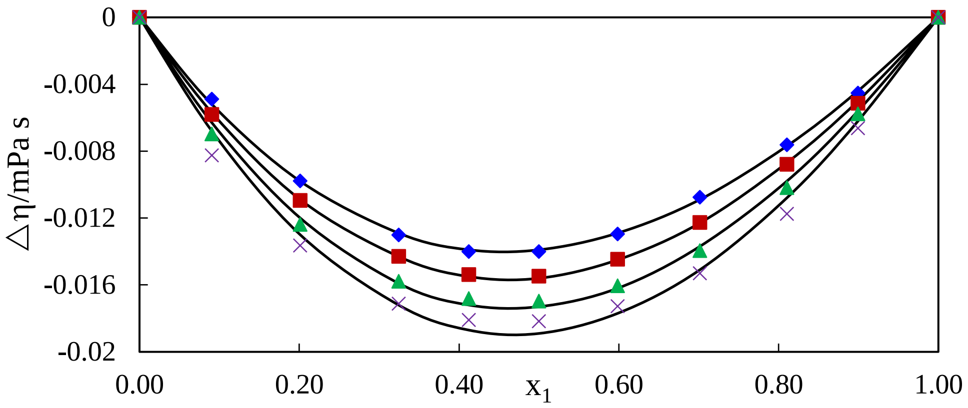

Fig.6. Deviation in viscosity (*Δη*) with mole fraction x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and solid lines have been drawn from R-K equation using the coefficients given in Table 3.

Figure 7 depicts the relationship between ΔG^{*E} and the mole fraction of DEC. As demonstrated in Fig.7, the ΔG^{*E} are positive throughout the composition at all temperatures. The ΔG^{*E} parameter is a valid criteria for detecting and interpreting the presence of interactions between dissimilar molecules. The significant positive values of ΔG^{*E} imply the establishment of intermolecular hydrogen bonding connections between DEC ions and 1,2-dichlorobenzene molecules. [30]. At all temperatures, the largest ΔG^{*E} is at 0.50 mole fraction of DEC. Decrease in ΔG^{*E} values are also observed with the increase in temperature.

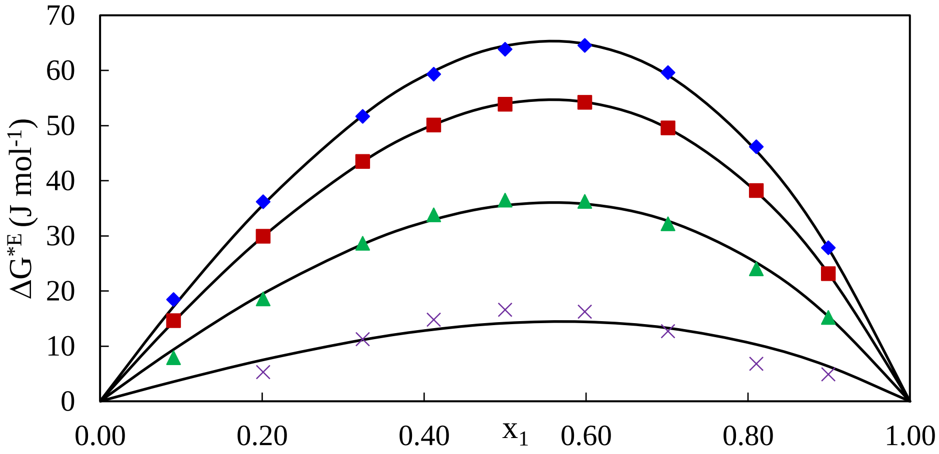

Fig.7. Excess Gibbs energy of activation (ΔG^{*E}) of viscous flow with mole fraction x_1 of DEC for DEC + 1,2-dichlorobenzene binary mixtures at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×. The points represent experimental values and solid lines have been drawn from R-K equation using the coefficients given in Table 3.

Partial molar properties

The values of partial molar properties, $\overline{V}^{\circ}_{\mathrm{m,1}}$ and $\overline{V}^{\circ}_{\mathrm{m,2}}$, $\overline{K}^{\circ}_{\mathrm{s,m,1}}$ and $\overline{K}^{\circ}_{\mathrm{s,m,2}}$, of DEC and 1,2-dichlorobenzene at infinite dilution were calculated by using the Eqs. (20)&(21), and the excess partial molar properties, $\overline{V}^{\circ \mathrm{E}}_{\mathrm{m,1}}$ and $\overline{V}^{\circ \mathrm{E}}_{\mathrm{m,2}}$, $\overline{K}^{\circ E}_{\mathrm{s,m,1}}$ and $\overline{K}^{\circ E}_{\mathrm{s,m,2}}$ at infinite dilution were calculated using the Eqs. (22) and (23) by substituting $\overline{V}^{\circ \mathrm{E}}_{\mathrm{m,1}}$ and $\overline{V}^{\circ}_{\mathrm{m,2}}$, $\overline{K}^{\circ E}_{\mathrm{s,m,1}}$ and $\overline{K}^{\circ E}_{\mathrm{s,m,2}}$ in place of $\overline{V}^{\mathrm{E}}_{\mathrm{m,1}}$ and $\overline{V}_{\mathrm{m,2}}$, $\overline{K}^{E}_{\mathrm{s,m,1}}$ and $\overline{K}^{E}_{\mathrm{s,m,2}}$ respectively. The values of $\overline{V}^{\circ}_{\mathrm{m,1}}$, $V^{*}_{\mathrm{m,1}}$, $\overline{V}^{\circ \mathrm{E}}_{\mathrm{m,1}}$, $\overline{V}^{\circ}_{\mathrm{m,2}}$, $V^{*}_{\mathrm{m,2}}$ and $\overline{V}^{\circ \mathrm{E}}_{\mathrm{m,2}}$ & $\overline{K}^{\circ}_{\mathrm{s,m,1}}$, $K^{*}_{\mathrm{s,m,1}}$, $\overline{K}^{\circ E}_{\mathrm{s,m,1}}$, $\overline{K}^{\circ}_{\mathrm{s,m,2}}$, $K^{*}_{\mathrm{s,m,2}}$, $\overline{K}^{\circ E}_{\mathrm{s,m,2}}$ for the binary mixtures at each investigated temperature are listed in Table 4 & 5 and the variations of $\overline{V}^{E}_{m,1}$, and $\overline{V}^{E}_{m,2}$ with composition at different temperatures are presented in Fig.8.

Table 4. The values $\bar{V}^{0}_{m,1}, \bar{V}^{*}_{m,1}, \bar{V}^{0E}_{m,1}, \bar{V}^{0}_{m,2}, \bar{V}^{*}_{m,2}, \bar{V}^{0E}_{m,2}$ of the components for DEC + 1,2-dichlorobenzene mixtures at 303.15-318.15 K from Redlich-Kister equation.

T/K	$10^6\bar{V}^{0}_{m,1} m^3 \cdot mol^{-1}$	$10^6\bar{V}^{*}_{m,1}$	$10^6\bar{V}^{0E}_{m,1}$	$10^6\bar{V}^{0}_{m,2}$	$10^6\bar{V}^{*}_{m,2}$	$10^6\bar{V}^{0E}_{m,2}$
303.15	122.20	122.61	-0.41	113.24	113.54	-0.30
308.15	122.88	123.33	-0.46	113.64	113.99	-0.35
313.15	123.57	124.07	-0.49	114.11	114.51	-0.40
318.15	124.29	124.82	-0.53	114.58	115.04	-0.47

Table 5. The values $\bar{\kappa}^{0}_{s,m,1}, \kappa^{*}_{s,m,1}, \bar{\kappa}^{0,E}_{s,m,1}, \bar{\kappa}^{0}_{s,m,2}, \kappa^{*}_{s,m,2} \mathit{and} \bar{\kappa}^{0,E}_{s,m,2}$ of for the components for DEC + 1,2-dichlorobenzene at 303.15-318.15 K.

T/K	$\bar{\kappa}^{0}_{s,m,1} dm^3TPa^{-1}mol^{-1}$ x10^{-14}	$\kappa^{*}_{s,m,1}$	$\bar{\kappa}^{0,E}_{s,m,1}$	$\bar{\kappa}^{0}_{s,m,2}$	$\kappa^{*}_{s,m,2}$	$\bar{\kappa}^{0,E}_{s,m,2}$
303.15	8.298	9.509	-1.211	3.958	5.498	-1.539
308.15	8.616	9.969	-1.353	4.002	5.720	-1.718
313.15	8.948	10.455	-1.507	4.047	5.973	-1.926
318.15	9.317	10.971	-1.654	4.032	6.221	-2.189

A thorough examination of the values of $\overline{V}^{E}_{m,1}$, and $\overline{V}^{E}_{m,2}$ & $\overline{K}^{E}_{s,m,1}$, and $\overline{K}^{E}_{s,m,2}$ Fig.8 reveals that they are all negative for the binary mixtures over the entire composition range. By this, the molar volumes of each component in the binary combination are fewer than their respective molar volumes in the pure state, implying that when DEC is mixed with 1,2-dichlorobenzene, the volume decreases. The negative $\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$ & $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ values, in general, indicate that there are considerable solute-solvent interactions between dissimilar molecules in the mixture. The DEC–DEC or 1,2-dichlorobenzene - 1,2-dichlorobenzene interactions are smaller than the DEC–1,2-dichlorobenzene interactions, as seen by the negative $\overline{V}^{E}_{m,1}$, and $\overline{V}^{E}_{m,2}$ & $\overline{K}^{E}_{s,m,1}$, and $\overline{K}^{E}_{s,m,2}$ values.

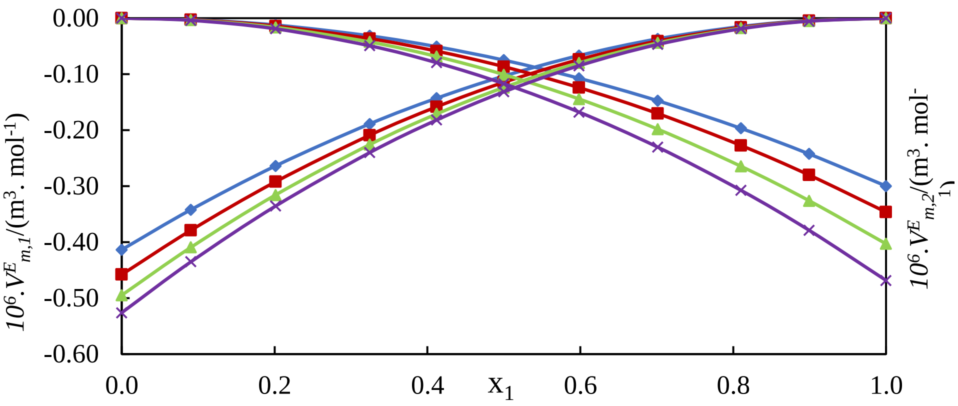

Fig. 8. Excess partial molar volume ($\overline{V}^E_{m,1}$ and $\overline{V}^E_{m,2}$) with mole fraction x_1 of DEC in the binary mixtures of DEC (1) with 1,2-dichlorobenzene (2) at temperatures, *T*/K = 303.15,♦; At *T*/K = 308.15,■; *T*/K = 313.15, ▲; *T*/K = 318.15, ×.

A deeper look at Tables 4 and 5 reveals that the values of $\overline{V}^{0,E}_{m,1}$ and $\overline{V}^{0,E}_{m,2}$ & $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ are negative for the binary systems at all investigated temperatures. This means that the molar volume of each component in a mixture is smaller than the corresponding molar volume, i.e. the combination of DEC and 1,2-dichlorobenzene leads in volume contracture. Negative excessive volumes of molar components ($\overline{V}^{0,E}_{m,1}$ and $\overline{V}^{0,E}_{m,2}$ & $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$) might be interpreted as an indication of unique interactions with molecular systems, as a result of interstitial accommodation, or as a signal of 1,2-dichlorobenzene assimilation into DEC cavities. Clathrate formation should be tightly related to a solution that fits into solvent structures and is proportional to the size of the co-solvents.

Table 6. Values of θ_2, χ_{12}, experimental and calculated V_m^E (using PFP theory) and three PFP contributions for near equimolar composition at T = (303.15 to 318.15) K.

T/K	θ_2	$10^{-7}.\chi_{12}$	10^6 V_m^E/m^3 mol^{-1}		PFP contributions to V_m^E		
		(J mol^{-1})	Expt.	PFP	Int.	fv.	Ip
303.15	0.4986	5.144	-0.0900	-0.0892	0.069	-0.2563	0.0981
308.15	0.4963	4.992	-0.1006	-0.1005	0.125	-0.1826	-0.0427
313.15	0.4943	4.864	-0.1103	-0.1122	0.131	-0.1212	-0.1223
318.15	0.4923	4.747	-0.1202	-0.1243	0.106	-0.0727	-0.1580

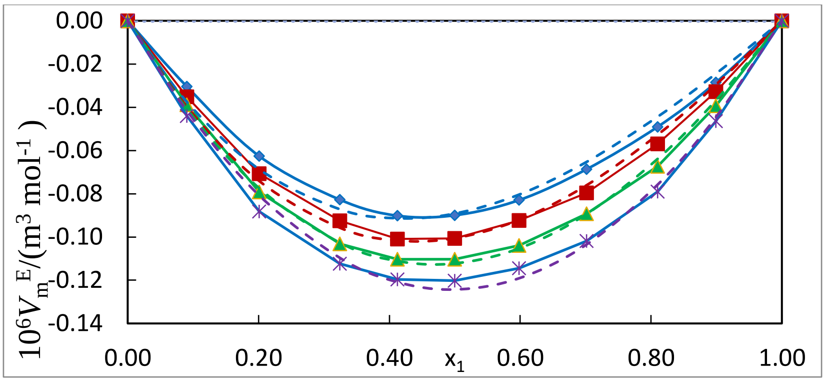

Fig.9. Plot of excess molar volume (V_m^E) against mole fraction of DEC with 1,2-dichlorobenzene at 303.15 K to 318.15 K. The corresponding dotted (---) curves have been derived from PFP theory. The corresponding solid curves have been derived experimental results.

Furthermore, in order to check whether χ_{12} derived from nearly equimolar V_m^E values can predict the correct composition dependence V_m^E has been calculated theoretically using χ_{12} over the entire composition range [31]. The theoretically calculated values are plotted in Fig.9 for comparison with the experimental results. Fig.9 shows that the PFP theory is quite successful in predicting the trend of the dependence of V_m^E on composition for the present system.

5. Conclusions

The excess molar volumes, excess isentropic compressibility, excess molar isentropic compressibility, excess isobaric thermal expansion, excess speed of sound, deviation in viscosity and excess Gibb's free energy of activation for viscous flow were calculated from the experimental values of density, speed of sound and viscosity at four temperatures of DEC with 1,2-dichlorobenzene over the whole composition range. These factors' sign and magnitude have been addressed in terms of the molecular interactions between the mixing components. Negative values of V_m^E, κ_s^E, $K_{s,m}^E$, α^E and $\Delta\eta$ and positive values of u^E and ΔG^{*E} are observed. At all temperatures, the largest ΔG^{*E} is at 0.50 mole fraction of DEC. The observed attributes are a combination of the interaction part and the size impact. The Prigogine-Flory-Patterson (PFP) theory also reveals that the selected system has high agreement between the estimated and experimental of V_m^E curves.

References

[1] P. Vasundhara, C. Narasimha Rao, L. Venkatramana, K. Sivakumar, P. Venkateswarlu, R.L. Gardas, “Thermodynamic properties of binary mixtures of aniline with halogenated aromatic hydrocarbons: Measurements and Correlations”. *J. Mol. Liq.* 202, (**2015)**, pp. 158-164.

[2] M. Narasaiah, K. Narendra, P. Bharath, T.S. Krishna, D. Ramachandran, “Excess speed of sound and excess molar isentropic compressibility in binary mixtures of selected amines in 2-methoxy ethanol at various temperatures”. *Phys. Chem. Res.* 10(3), (**2022)**, 379-390.

[3] L. Venkataramana, R.L. Gardas, K. Sivakumar, K. Dayananda Reddy, “Thermodynamics of binary mixtures: The effect of substituents in aromatics on their excess properties with benzylalcohol”. *Fluid Phase Equilib.* 367, (**2014)**, 7-21.

[4] J. V. Srinivasu, T. S. Krishna, K. Narendra, G. Srinivasa Rao, B. Subba Rao, “Elucidation of H-bond and molecular interactions of 1,4-butanediol with cresols: acoustic and volumetric data”. *J Mol. Liq.* 236, (**2017)**, 27-37.

[5] A. Venkateswara Rao, K. Narendra, T. Srinivasa Krishna, P. Bharat, D. Ramachandran, “Study of molecular interactions of fossil fuels through acoustic and volumetric data”. *Phys. Chem.Res.* 11, (**2023)**, 129–137.

[6] Zhiyuan Zeng; Wen-I Liang; Hong-Gang Liao; Huolin L Xin; Yin-Hao Chu et al., “Visulization of electrode-electrolyte interfaces in $LiPF_6$/EC/DEC electrolyte for Lithium ion batteries via in Situ TEM”. *Nano Letters* 14, (**2014)**, 1745−1750.

[7] https://www.azom.com/news.aspx?newsID=48183 dt: 19th Sep 2017.

[8] Kirk-Othmer, Encyclopedia of Chemical Technology, 5th edn, Wiley Inter Sceince, New York, **2004**, p.224.

[9] V. Syamala, D. Rajasekhar, K. Sivakumar, P. Venkateswarlyu, “Volumetric, ultrasonic and transport properties of binary liquid mixtures containing dimethyl formamide at 303.15 K”. *Chin. J. Chem*. 25, (**2007)**, 32-43.

[10] E.R. Lopez, L. Lugo, M. J. P. Comunas, J. Garcia, J. Fernandez, “Temperature dependence of the excess molar volume of (dimethyl carbonate or diethyl carbonate + toluene) from T = 278.15 K to 323.15 K”. *J. Chem. Thermodyn.* 32, (**2000)**, 743-754.

[11] L. Mosteiro, E. Mascato, B.E. de Cominges, T.P. Iglesias, J.L. Legido, “ Density, speed of sound, refractive index and dielectric permittivity of (diethyl carbonate + n-decane) at several temperatures”. *J. Chem. Thermodyn*. 33, (**2001)**, 787-801.

[12] Song, W.; Zhang, H.; Yang, Z.; Wang, J.; Yue, Z.; Ji Yu Z., “Intermolecular Interaction for Binary Mixtures of Propylene Carbonate with Acetonitrile, Dimethyl Carbonate, Diethyl Carbonate at Different Temperatures: Density and Viscosity”. *Zeitschrift für Physikalische Chemie* 232(1), (**2017)**, 127–151.

[13] Rodrıguez, A. Canosa J.; Tojo. J., “Physical properties of the binary mixtures (diethyl caronate + hexane, heptanes, octane and cyclohexane) from T = 293.15 K to T = 313.15 K”. *J. Chem. Thermodyn.* 35, (**2003)**, 1321-1333.

[14] Mosteiro, L.; Casas, L. M.; Jose L Legido., “Surface tension, density and speed of sound for the ternary mixture {diethyl carbonate + p-xylene + decane}”. *J. Chem. Thermodyn.* 41, (**2009)**, 695-704.

[15] Mou, L.; Chai, Y.; Yang, G.; Xia, Q.; Liu, Q.; Zheng, Q.; Zhang, Q., "Density and viscosity of four binary mixtures of [C_2mmim][NTf_2]/[C_4mmim][NTf_2] + dimethyl carbonate/diethyl carbonate". *J. Chem. Thermodyn.* 130, (**2019)**, 183-191.

[16] Ana B Pereiro.; Rodriguez, A.; Canosa, J.; Tojo, J., "Density, viscosity and speed of sound of dialkyl carbonates with cyclopentane and methyl cyclohexane at several temperatures". *J. Chem. Eng. Data.* 49, (**2004)**, 1392-1399.

[17] Ratnam, M. V.; Sudhir, M.; Nandini, M., "Excess properties of diethyl carbonate + ketone binary mixtures at variable temperatures: Application of PFP theory to excess volumes". *J. Mol. Liq.* 177, (**2013)**, 229-236.

[18] Rivas, M, A.; Pereira, S, M.; Benerji, N.; Iglesias, T. P., "Permittivity and density of binary systems of {dimethyl or diethyl carbonate} + n-dodecane from T = (288.15 to 328.15)K". *J. Chem. Thermodyn.* 36, (**2004)**, 183-191.

[19] Rao, V. S.; Reddy, M. S.; Rao, A. S.; Raju, G. P.; Raju, K. T. S. S.; Hari Babu, B., "Volumetric, acoustic, optical and spectroscopic studies of binary mixtures of the ionic liquid, 1-butyl-3-methyl imidazolium bis(tri fluoro methyl sulfonyl) imide and diethyl carbonate". *Phy. Chem. Liq.* 56, (**2018)**, 332-352.

[20] Bhatia, S. C.; Sangwan, J.; Rani, R.; Bhatia, R., "Densities, viscosities, speeds of sound and refractive indices of binary mixtures of 2-octanol with chlorobenzene". *Int. J. Thermophys.* 56, (**2011)**, 1669-1674.

[21] Baragi, J.G.; Aralaguppi, M.I.; Aminabhavi, T.M.; Kariduraganavar, M.Y.; Kulkarni, S.S., "Density, Viscosity, Refractive Index, and Speed of Sound for Binary Mixtures of 1,4-Dioxane with Different Organic Liquids at (298.15, 303.15, and 308.15) K". *J. Chem. Eng. Data* 50, (**2005)**, 917-923.

[22] Venkatramana, L.; Sivakumar, K.; Govinda, V.; Dayananda Reddy, K., "Study on solution properties of some industrially important solvents with an aromatic alcohol". *J. Mol. Liq.* 186, (**2013)**, 163-170.

[23] Yang, C.; Yu, W.; Tang, D., "Densities and viscosities of binary mixtures of m-cresol with ethylene glycol or methanol over several temperatures". *J. Chem. Eng. Data* 51, (**2006)**, 935-939.

[24] Douheret, G.; Davis, M. I.; Reis, J. C., "Excess isentropic compressibilities and excess ultrasound speeds in binary and ternary liquid mixtures". *Fluid Phase Equilib.* 231, (**2005)**, 246–249.

[25] Benson, G. C.; Kiyohara, O., "Evaluation of excess isentropic compressibilities and isochoric heat capacities". *J. Chem. Thermodyn*. 11, (**1979)**, 1061–1064.

[26] Redlich, O.; Kister, A. T., "Algebraic representation of thermodynamic properties and the classification of solutions". *Ind. Eng. Chem.* 40, (**1948)**, 345–348.

[27] B. Jacobson, "Ultrasonic velocity in liquid mixtures". *J. Chem. Phys*. 20, (**1952)**, 927-928.

[28] S.C. Bhatia, J. Sangwan, R. Rani, R. Bhatia, "Densities, viscosities, speeds of sound and refractive indices of binary mixtures of 2-octanol with chlorobenzene". *Int. J. Thermophys*. 32, (**2011)**, 2027-2039.

[29] S. Oswal, H.S. Desai, "Studies of viscosity and excess molar volume of binary mixtures: 1-propylamine+1-alkanol mixtures at 303.15 and 313.15 K". *Fluid Phase Equilib*. 149, (**1998)**, 359-376.

[30] U.R Kapadi, D.G. Hundiwale, N.B. Patil, M.K. Lande, P.R. Patil, “Studies of viscosity and excess molar volume of binary mixtures of propane-1,2 diol with water at various temperatures”. *Fluid Phase Equilib*. 192, (**2001)**, 63-70.

[31] T. Srinivasa Krishna, K. Narendra, M. Gowrisankar, A.K. Nain, B. Munibhadrayya, “Physicochemical and spectroscopic studies of molecular interactions of 1-butyl-3-methylimidazolium hexafluorophosphate + 2-methoxyethanol or 2-ethoxyethanol binary mixtures at temperatures from 298.15 to 323.15 K”. *J Mol Liq*. 227, (**2017)**, 333-350.