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Investigation of molecular interactions in binary mixture of dimethyl carbonate + *N*-methylformamide at T = (303.15, 308.15, 313.15 and 318.15) K

Thermo-physical and spectroscopic study

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Abstract
Density (ρ) and speed of sound (u) of binary liquid mixtures of dimethyl carbonate and *N*-methylformamide have been determined at T = (303.15, 308.15, 313.15 and 318.15) K over the entire composition range. Experimental data are used to evaluate excess values of molar volume (V_m^E), isentropic compressibility (k_s^E), isothermal compressibility (k_T^E), intermolecular free length (L_f^E), acoustic impedance (Z^E) and ultrasonic speed (u^E). The V^E data in the present investigation were analysed by using Prigogine–Flory–Patterson (PFP) theory. Partial and excess partial molar volumes ($\bar{V}_{m,1}$, $\bar{V}_{m,2}$), ($\bar{V}_{m,1}^E$, $\bar{V}_{m,2}^E$) and partial and excess partial molar volume of the components at infinite dilution ($\overline{V}_{m,1}^{\infty}$, $\overline{V}_{m,2}^{\infty}$), ($\overline{V}_{m,1}^{E,\infty}$, $\overline{V}_{m,2}^{E,\infty}$) at T = (303.15, 308.15, 313.15, 318.15) K have been calculated. The excess/deviation properties were fitted to Redlich–Kister equation to obtain their coefficients and standard deviations. The present investigation also comprises the acoustic non-linearity parameter (B/A) in the mixtures and calculation of cohesive energy ΔA, Van der Wall's constants (a, b) and distance of closest approach (d). Moreover, various semi-empirical relations of ultrasonic speed have been used to correlate the theoretical velocities. FT-IR spectra of pure components and their binaries have been measured at T = 298.15 K.

Keywords Excess molar volume · Partial molar volumes · Isentropic compressibility · PFP theory · FT-IR spectra

Introduction

The thermo-physical properties of pure liquids and liquid mixtures are studied for many reasons, most important of which is to provide information about molecular interactions in liquid mixtures [1], which are having immense use in theoretical and practical considerations. In practical aspect, the density is necessary in lot of chemical engineering calculations such as in designing the dimensions of boilers, condensers and storage deposits, etc. [2, 3]. Ultrasonic studies of liquid mixtures can be used to determine the effect of structure of donor molecules and polarity of medium on the stability of complexes which play a significant role in complexation [4] and formation of constant values of charge transfer complexes to compare their stabilities [5]. With the wide range of requisite properties, binary and multi-component liquid mixtures rather than pure liquids are of great importance in several chemical, industrial and biological processes [6].

The liquids in the present system are chosen based on their industrial importance. Dimethyl carbonate (DMC) is a benign biodegradable chemical that it is investigated as substitute of methyl *tert*-butyl ether in fuels [7]. DMC has

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been used in lithium battery technology [8]; it is a strong contender in gasoline industry, and it has both low toxicity and relatively quick biodegradability [9, 10]. *N*-methylformamide (NMF) having anticancer properties is used in pharmaceutical industry and organic synthesis [11]. NMF, the monomethylated formamide, is a protic dipolar solvent possessing the donor (–CO) and acceptor (–NH) groups of amides, thus forming a linear hydrogen-bonded structure. Several applications associated with these solvents prompted the need of further extensive information on the thermodynamic and acoustic properties of these solvents and their mixtures. Hence, an attempt has been made to study the molecular interactions in the binary system (DMC + NMF) at T = (303.15, 308.15, 313.15 and 318.15) K. Considerable work has been reported [12–15] on ultrasonic and volumetric studies of DMC as one of the components in binary liquid. Literature survey reveals that no work has been reported on the binary mixture of dimethyl carbonate and *N*-methylformamide.

Experimental

Chemicals

Dimethyl carbonate and *N*-methylformamide (A.R. grade) were purchased from Sigma-Aldrich, India, with stated purity 99%. The suppliers and purity of component liquids are reported in Table 1. The chemicals were further purified as described in the literature [16]. The pure chemicals were stand over activated 0.4-nm molecular sieves and stored in dark bottles. The chemicals after purification were 99.7% pure, and their purity was ascertained by the GLC and also by comparing experimental values of density and speed of sound with those reported in the literature [17–23] at T = (303.15, 308.15, 313.15, 318.15) K; this comparison is given in Table 2, and agreement between the experimental and the literature values is found to be good.

Apparatus and procedure

Jobs method of continuous variation was used to prepare mixtures in required proportions. The binary mixtures are prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm$ 1 $\times$ 10^{-7} kg and by syringing each component into airtight stopper bottle to minimise evaporation losses. The uncertainty on mole fraction is estimated to be $\pm$ 1 $\times$ 10^{-4}. After thorough mixing of liquids, the flasks were left undisturbed to attain thermal equilibrium. The densities (ρ) of pure liquids and their mixtures are determined using a 10^{-5} m^3 double-arm pycnometer, and the values from triplicate replication at each temperature are reproducible within 2 $\times$ 10^{-1} kg m^{-3}. The pycnometer was calibrated using conductivity water with 995.61 kg m^{-3} as its density at 303.15 K. Travelling microscope is used to record the position of the liquid levels in the two arms of the pycnometer (which is made sure that it is free of air bubbles) could be read to 0.01 mm. The repeatabilities in the measured parameter of density are 3 in 10^4 parts and in mole fraction is $\pm$ 0.0002. Temperature control for the measurement of density is achieved by using a microprocessor-assisted circulating water bath, (supplied by Mac, New Delhi) regulated to $\pm$ 0.01 K, with proportional temperature controller. Adequate precautions were taken to minimise evaporation losses during the actual measurements. Speed of sound (u) in pure liquids and in their binary mixtures is measured using a single-crystal variable path multi-frequency ultrasonic interferometer (Mittal Enterprises, New Delhi, M-81 Model), operated at a frequency of 2 MHz. The uncertainty in the ultrasonic speed measurement is found to be $\pm$ 0.5 m s^{-1}. The temperature was maintained by circulating water around the liquid cell from a U10 thermostat controlled to $\pm$ 0.01 K.

Theory

The experimentally measured values of and u were used to calculate the thermodynamic and acoustical parameters using the following standard equations.

Molar volume (V_m) is evaluated with the equation

$$V_m = M_1x_1 + M_2x_2/\rho. \quad (1)$$

M_1 and M_2 are the molar masses of pure components, x_1 and x_2 are the mole fractions for the binary mixture components [dimethyl carbonate (1) + *N*-methylformamide (2)], and ρ is the density of medium. Partial molar volume is an extensive property which depends on the phase composition at constant pressure and temperature. Partial

Table 1 List of chemicals with details of Provenance, CAS number and mass fraction purity

Chemical	Provenance	CAS number	Purification method	Mass fraction purity	Analysis method
Dimethyl carbonate	Sigma-Aldrich, India	61638-6	Distillation	0.99	Gas liquid chromatography
N-methylformamide	Sigma-Aldrich, India	123-39-7	Distillation	0.99	Gas liquid chromatography

Table 2 Comparison of experimental values of density, ρ, ultrasonic speed of sound, u of pure liquids at atmospheric pressure with the corresponding literature values at different temperatures

Component	$\rho/10^3$ kg m^{-3}		u/m s^{-1}		C_p/J K^{-1} mol^{-1}	
	Expt.	Litt.	Expt.	Litt.	Fitted	Litt.
Dimethyl carbonate						
303.15 K	1.0567	1.056719 [17]	1176	1177.0 [18]	165.63	–
308.15 K	1.0501	1.050071 [17]	1155	1153.7 [19]	166.30	166.30 [20]
313.15 K	1.0434	1.043388 [17]	1135	1135.0 [18]	167.04	–
318.15 K	1.0371	1.036687 [17]	1116	–	167.84	–
N-methylformamide						
303.15 K	0.9956	0.99449 [21]	1408.8	1408.5 [22]	125.10	125.1 [23]
308.15 K	0.9905	0.99001 [21]	1398.9	1398.2 [22]	126.20	126.2 [23]
313.15 K	0.9855	0.98547 [21]	1381.6	1382.5 [22]	127.30	–
318.15 K	0.9801	0.98088 [21]	1365.5	1365.8 [22]	128.40	–

Available C_p values for DMC at 288.15 K—164.03 [20]; at 298.15 K—165.30 [20]

Available C_p values for NMF at 298.15 K—124.0 [23]

molar volumes of components 1 and 2 $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ in the binary mixtures are calculated using the following equations:

$$\bar{V}_{m,1} = V_m^E + V_1^0 + (1 - x_1)\left(\partial V_m^E/\partial x_1\right)_{T,P} \quad (2)$$

$$\bar{V}_{m,2} = V_m^E + V_2^0 - x_1\left(\partial V_m^E/\partial x_1\right)_{T,P}. \quad (3)$$

Here V_1^0, V_2^0 are the molar volumes of components DMC and cresols, respectively, and x_1 represents mole fraction of former component. The $\left(\partial V_m^E/\partial x_1\right)_{T,P}$ value was calculated by the differentiation of the polynomial fitting of V_m^E equation with respect to x_1. The values of partial molar volumes of pure components are used to calculate the excess partial molar volumes using the equations:

$$\bar{V}_{m,1}^E = \bar{V}_{m,1} - V_1^0 \quad (4)$$

$$\bar{V}_{m,2}^E = \bar{V}_{m,2} - V_2^0. \quad (5)$$

The partial molar volumes and excess partial molar volumes of the components at infinite dilution $\bar{V}_{m,1}^{\infty}$, $\bar{V}_{m,2}^{\infty}$, $\bar{V}_{m,1}^{E,\infty}$ and $\bar{V}_{m,2}^{E,\infty}$, respectively, are given by

$$\bar{V}_{m,1}^{E,\infty} = A_0 + A_1 + A_2 + A_3 + \cdots = \bar{V}_{m,1}^{\infty} - V_1^0 \quad (6)$$

$$\bar{V}_{m,2}^{E,\infty} = A_0 + A_1 + A_2 + A_3 + \cdots = \bar{V}_{m,2}^{\infty} - V_2^0. \quad (7)$$

Here A_0, A_1, A_2, $A_{3\ldots}$ are *R–K* coefficients.

The isentropic compressibility, κ_S, is computed directly from the measured values of speed of sound and density using the Newton–Laplace equation [24, 25]

$$k_s = \left(\frac{1}{\rho u^2}\right). \quad (8)$$

Isothermal compressibility, K_T, can be evaluated from

$$k_T = k_s + \frac{TV_m\alpha_P^2}{C_P}. \quad (9)$$

The isobaric thermal expansion coefficient, α_P, values for the mixtures were calculated from temperature dependence of density data which is defined by

$$\alpha_P = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_{P,x_i}. \quad (10)$$

C_P is the heat capacity of the mixture and C_P values for the mixtures have been calculated from specific heats of pure liquids by using the relation

$$C_p^{id} = x_1C_{p,1} + x_2C_{p,2}. \quad (11)$$

For the present scenario, the literature values of C_P are not available at all temperatures. Hence, from the available literature values, required C_P values at T = (303.15, 308.15, 313.15, 318.15) K are taken by fitting C_P and T.

The intermolecular free length is calculated using the expressions [26]

$$L_f = \frac{K}{u\rho^{\frac{1}{2}}}, \quad (12)$$

where K is the temperature-dependent Jacobson constant, which varies with square root of absolute temperature, and its values are given by $K = (93.875 + 0.375\ T)\ 10^{-8}$.

The acoustic impedance, Z, is calculated using the expression [26]

$$Z = u\rho \quad (13)$$

Excess/deviation properties such as V_m^E and k_T^E have been calculated using the following equation:

$$Y^E \text{ or } Y = Y_{mix} - (x_1Y_1 + x_2Y_2). \quad (14)$$

Excess isentropic compressibility is given by

$$\kappa_s^E = \kappa_s - \kappa_s^{id}, \tag{15}$$

where K_s is the isentropic compressibility and κ_S^{id} is the isentropic compressibility of the ideal mixture, which is calculated in the manner as suggested by Benson and Kiyohara [27].

$$\kappa_S^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{S,i} + \frac{TV_i\alpha_i^2}{C_{p,i}}\right] - \left\{T\frac{\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \phi_i \alpha_i\right)^2}{\left(\sum_{i=1}^{2} x_i C_{p,i}\right)}\right\}, \tag{16}$$

where ϕ_i is the volume fraction of the ith component and is given by $\phi_i = \frac{x_i V_i}{\sum_{i=1}^{2} x_i V_i}$, T is the temperature, $\kappa_{s,i}$ is the isentropic compressibility, V_i is the molar volume, α_i is the isobaric thermal expansion coefficient, and $C_{P,i}$ is the heat capacity of the ith component.

The excess values of speed of sound are calculated from

$$u^E = u - u^{id} = u - \left(\rho^{id} k_s^{id}\right)^{-\frac{1}{2}}. \tag{17}$$

These excess or deviation properties were fitted to Redlich–Kister-type polynomial equation [28] by using the following formulae:

$$Y_{cal}^E = x_1 x_2 \sum_{i=1}^{n} A_{i-1}(x_2 - x_1)^{i-1}. \tag{18}$$

The coefficients of A_{i-1} in the above equation along with the standard deviation σ (Y^E) have been calculated. These coefficients are the adjustable parameters to get best-fit values of Y_{cal}^E. The standard deviations σ of Y_{cal}^E are calculated by using the relation:

$$\sigma = \left[\Sigma\left(Y_{expt}^E - Y_{cal}^E\right)^2/(m-n)\right]^{1/2}, \tag{19}$$

where m is the number of experimental data points, n is the number of coefficients considered, and Y_{cal}^E have been obtained from Eq. (18) using the best-fit values of A_{i-1}.

Results and discussion

The study of excess parameters rather than actual values is useful to elucidate nature of molecular interactions between the components of liquid mixtures. Excess values in terms of thermodynamic and acoustic studies are necessary for the better understanding of nature of liquid components in binary/multi-component systems. When we mix two or more solvents, the surrounding atmosphere of individual components will change depending on the ability to interact with the other component. During the mixing process, there are some intermolecular forces which decide the type of interaction (dispersion/attraction) present among the components of mixtures.

The experimental values of density (ρ) and speed of sound (u) of the binary mixture (DMC + NMF) at temperatures (303.15, 308.15, 313.15, and 318.15) K are presented in Table 3. From Table 3, it is observed that u values decrease and ρ values increase with the composition of the DMC and with increase in temperature. This non-linear variation of u and ρ of binary mixture with mole fraction of DMC and temperature is the deviation from ideal behaviour and further confirms the presence of specific interactions among the components of hetero-molecules.

Excess/deviation properties are useful in evaluation of type of interaction present among the components of liquid. In this study, we have calculated several excess/deviation parameters over the entire composition range of DMC at T = (303.15, 308.15, 313.15, 318.15) K. Further, we have correlated the results obtained from excess/deviation properties to explain the nature of molecular interactions in the binary system of DMC + NMF.

Volumetric studies

The values of excess molar volume, V_m^E, for the binary mixture [dimethyl carbonate (1) + N-methylformamide (2)] for various mole fractions of DMC at T = (303.15, 308.15, 313.15, 318.15) K are listed in Table 3. An examination of V_m^E curves from Fig. 1 shows that V_m^E values exhibit negative deviation from ideality over the entire composition of DMC for binary mixture (DMC + NMF). The values of V_m^E become more negative as the temperature increases from 303.15 to 318.15 K. Further, negative values of V_m^E suggest that factors which are contributing in contraction of volume are dominant in the binary liquid at all the temperatures investigated and the order of strength of strong interactions with increasing temperature is as follows: (303.15 < 308.15 < 313.15 < 318.15) K.

It has been reported that the V_m^E values result from the contributions due to the physical, chemical and structural characteristics of the component liquids [29–31]. The physical contributions comprise dispersion forces and weak non-specific interactions which include breaking of the structure of one or both the components in the solution, loss of dipolar association among the components of molecules, steric hindrance of the molecules and H-bond rupture which lead to positive V_m^E values [32, 33]. Chemical interactions comprise specific type of interactions like dipole–dipole, dipole–induced dipole, formation of charge transfer (donor–acceptor) complexes, H-bonding between the component molecules which result in negative values of V_m^E. The structural contributions arose from difference in

Table 3 Experimental values of density (ρ), velocity (u), calculated excess molar volume (V_m^E), partial molar volumes ($\bar{V}_{m,1}$, $\bar{V}_{m,2}$) and excess partial molar volumes ($\bar{V}_{m,1}^E$, $\bar{V}_{m,2}^E$) of the components against mole fraction (x_1) of DMC for binary mixture [dimethyl carbonate (1) + *N*-methylformamide (2)] at T = (303.15, 308.15, 313.15 and 318.15) K

x_1	$\rho/10^3$ kg m^{-3}	u/m s^{-1}	V_m^E /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,1}$ /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,2}$ /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,1}^E$ /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,2}^E$ /10^{-6} m^3 mol^{-1}
303.15 K							
0.0000	0.9956	1408.8	0.0000	83.5174	59.3305	− 1.7281	0.0000
0.0718	1.0050	1393.0	− 0.1984	83.8289	59.2419	− 1.4167	− 0.0885
0.1482	1.0139	1376.2	− 0.3782	83.5713	59.1890	− 1.6742	− 0.1415
0.2297	1.0229	1358.1	− 0.5693	83.2751	59.2886	− 1.9705	− 0.0419
0.3169	1.0312	1338.6	− 0.7272	83.2595	59.4243	− 1.9860	0.0938
0.4104	1.0385	1317.5	− 0.8285	83.6120	59.3507	− 1.6336	0.0202
0.5107	1.0442	1294.4	− 0.8299	84.2048	58.8812	− 1.0408	− 0.4492
0.6189	1.0479	1268.9	− 0.6839	84.7844	58.1103	− 0.4611	− 1.2202
0.7357	1.0506	1240.7	− 0.4544	85.1246	57.4934	− 0.1210	− 1.8370
0.8623	1.0533	1209.9	− 0.2063	85.2145	57.2190	− 0.0310	− 2.1114
1.0000	1.0567	1176.0	0.0000	85.2456	54.4756	0.0000	− 4.8549
308.15 K							
0.0000	0.9905	1398.9	0.0000	83.1970	59.6365	− 2.5877	0.0000
0.0718	1.0010	1382.5	− 0.2787	83.8570	59.5178	− 1.9277	− 0.1187
0.1482	1.0102	1365.1	− 0.4895	83.7854	59.4189	− 1.9993	− 0.2176
0.2297	1.0190	1346.1	− 0.6856	83.5895	59.4910	− 2.1952	− 0.1456
0.3169	1.0270	1325.7	− 0.8368	83.6345	59.6158	− 2.1501	− 0.0207
0.4104	1.0342	1303.6	− 0.9465	84.0252	59.5309	− 1.7595	− 0.1056
0.5107	1.0397	1279.5	− 0.9409	84.6328	59.0498	− 1.1519	− 0.5868
0.6189	1.0431	1252.8	− 0.7887	85.2043	58.3171	− 0.5803	− 1.3194
0.7357	1.0456	1223.3	− 0.5592	85.5390	57.8799	− 0.2457	− 1.7567
0.8623	1.0477	1190.8	− 0.2777	85.6771	57.8872	− 0.1076	− 1.7493
1.0000	1.0501	1155.0	0.0000	85.7847	54.7275	0.0000	− 4.9090
313.15 K							
0.0000	0.9855	1381.6	0.0000	82.5572	59.9409	− 3.7766	0.0000
0.0718	0.9961	1365.0	− 0.2969	83.8321	59.8056	− 2.5017	− 0.1354
0.1482	1.0060	1347.6	− 0.5680	84.0830	59.6735	− 2.2508	− 0.2675
0.2297	1.0149	1328.6	− 0.7795	84.0025	59.7180	− 2.3313	− 0.2229
0.3169	1.0230	1308.1	− 0.9568	84.0459	59.8345	− 2.2880	− 0.1064
0.4104	1.0302	1285.9	− 1.0779	84.4015	59.7579	− 1.9323	− 0.1830
0.5107	1.0351	1261.4	− 1.0550	85.0045	59.2749	− 1.3293	− 0.6660
0.6189	1.0383	1234.5	− 0.9016	85.6282	58.4728	− 0.7056	− 1.4682
0.7357	1.0404	1204.5	− 0.6507	86.0472	57.8145	− 0.2866	− 2.1265
0.8623	1.0422	1171.6	− 0.3649	86.2364	57.3731	− 0.0974	− 2.5679
1.0000	1.0434	1135.0	0.0000	86.3338	53.5768	0.0000	− 6.3641
318.15 K							
0.0000	0.9801	1365.5	0.0000	82.8118	60.2679	− 4.0458	0.0000
0.0718	0.9915	1349.0	− 0.3563	83.8339	60.1752	− 3.0237	− 0.0928
0.1482	1.0018	1331.5	− 0.6584	84.1549	60.0726	− 2.7027	− 0.1953
0.2297	1.0110	1312.5	− 0.9028	84.2421	60.0687	− 2.6155	− 0.1992
0.3169	1.0193	1291.8	− 1.1034	84.4103	60.0881	− 2.4473	− 0.1799
0.4104	1.0260	1269.3	− 1.2032	84.7989	59.9438	− 2.0587	− 0.3241
0.5107	1.0306	1244.6	− 1.1656	85.3752	59.4699	− 1.4824	− 0.7980
0.6189	1.0336	1217.2	− 1.0074	85.9880	58.6760	− 0.8696	− 1.5920
0.7357	1.0356	1187.0	− 0.7622	86.4645	57.7966	− 0.3931	− 2.4713

Table 3 (continued)

x_1	$\rho/10^3$ kg m^{-3}	u/m s^{-1}	V_m^E /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,1}$ /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,2}$ /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,1}^E$ /10^{-6} m^3 mol^{-1}	$\bar{V}_{m,2}^E$ /10^{-6} m^3 mol^{-1}
0.8623	1.0368	1153.3	− 0.4280	86.7407	56.8066	− 0.1169	− 3.4614
1.0000	1.0371	1116.0	0.0000	86.8576	53.3651	0.0000	− 6.9028

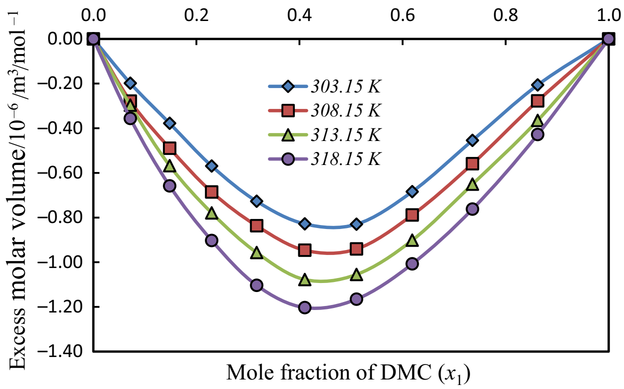

Fig. 1 Variation of excess molar volume (V_m^E) against mole fraction (x_1) of DMC for binary mixture [dimethyl carbonate (1) + *N*-methylformamide (2)] at T = 303.15 K (blue filled diamond), 308.15 K (red filled square), 313.15 K (green filled triangle) and 318.15 K (purple filled circle). (Color figure online)

molar volume and free volume of the components, which allows the interstitial accommodation and geometrical fitting of one component into the other, producing negative sign to V_m^E values.

A plausible qualitative interpretation of existing interaction in liquid components in the present binary system has been analysed. Dimethyl carbonate is a polar aprotic solvent with a dipole moment (μ = 0.90 D). *N*-methylformamide is a polar, protic solvent with very high dipole moment (μ = 3.86 D) [11]. NMF belongs to the amide group and has donor–acceptor O=C–N(H) (peptide) group in it, and its molecules in pure form are self-associated through dipole–dipole interactions, inter- as well as intra-molecular hydrogen bonding which makes the liquid structure becomes more ordered. High dipole moments associated with the NMF molecules may attract DMF molecule, which gives the possibility of Keesom-type interactions (attractive interactions between dipoles). According to Rajagopal and Chenthilnath [34], the strength of interaction between the participating molecules also depends on the dipole moment of the interacting molecules. In the present study, possibility of Keesom-type Van der Waals forces which arises due to dipole moment of components gives strong interactions leading to negative values of V_m^E [35]. Hence, it is assumed that dipole–dipole interactions are present among the liquid mixture of DMC and NMF.

Negative values of V_m^E are also attributed due to specific type of acid–base interactions between DMC and NMF molecules by considering *N*-methylformamide as Lewis base and dimethyl carbonate as Lewis acid. Nam-Tan [36] emphasised the importance of acid–base interaction to evaluate the interaction energy of alcohol–amine system. Balaji et al. [37] reported the existence of specific acid–base interactions between *N*-methyl formamide and ketone molecules to explain the nature of interaction. Since NMF has high dielectric constant value ε = 182.4 at 25 °C [38], it can act as good electron donor and can easily form complexes with other component of binary liquid. It is also possible that addition of DMC to the *N*-methylformamide may induce the mutual dissociation of hydrogen-bonded structures between the NMF and NMF molecules and subsequent formation of new hydrogen bond (> C=O:···HN <) between lone pair of electrons of proton acceptor oxygen atom of > C=O group of DMC and proton of > N–H group of NMF. The first effect causes increase in volume, and second effect decrease in volume. However, the actual volume change depends upon relative strength of these two effects. However, formation of hydrogen bonding phenomenon is more pronounced which is substantiated by the considerable contraction in volume producing negative values of V_m^E in the studied binary mixture [39]. Figure 2 shows possibility of H-bond formation between DMC and NMF.

With respect to the structural contribution, molar volumes of pure components DMC and NMF are 85.2456 (× 10^{-6} m^3 mol^{-1}) and 59.3274 (× 10^{-6} m^3 mol^{-1}) at 303.15 K, respectively, which might allow the component molecules to fit into each others' structures, thereby reducing the volume of the mixture. This phenomenon was

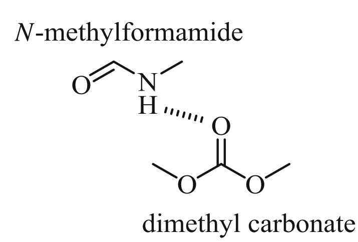

Fig. 2 Schematic representation of possible H-bonding in (DMC + NMF) binary mixture

also reported by others for interpreting negative V_m^E values [40, 41]. Further, from Table 3 it is observed that at ~ 0.5 mol fraction of DMC, V_m^E values change from − 0.8299 (× 10^{-6} m^3 mol^{-1}) to − 1.1656 (× 10^{-6} m^3 mol^{-1}) as the temperature increases from 303.15 to 318.15 K, i.e. magnitude of V_m^E values increases; this trend explains that with increase in temperature, strength of interaction among the liquid components increases. Rastogi et al. [42] reported that, as temperature increases, thermal energy activates the molecules; this would increase the rate of association between unlike molecules [43]. In short, in the present binary mixture, the observed negative values of V_m^E are the result of cumulative effect of all the above-mentioned factors such as dipole–dipole interactions, acid–base interactions, H-bonding, and interstitial accommodation of NMF molecules into voids of DMC molecules leading to the strength of interaction follows the order: (318.15 > 313.15 > 308.15 > 303.15) K.

The existing interactions in the liquid mixtures are well reflected in their partial molar volume studies. From Table 3, we observe that the values of $\bar{V}_{m,1}$ and $\overline{V}_{m,2}$ for both the components in the mixtures are lower than their individual molar volumes in the pure state, which indicates

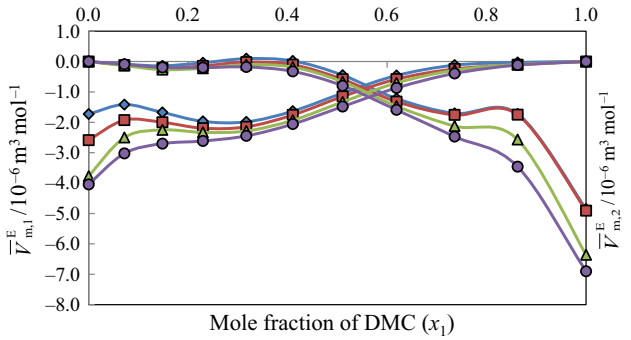

Fig. 3 Variation of excess partial molar volume of DMC ($\bar{V}^E_{m,1}$) and NMF ($\bar{V}^E_{m,2}$) against mole fraction (x_1) of DMC in binary mixture [dimethyl carbonate (1) + *N*-methylformamide(2)] at temperatures *T* = 303.15 K (blue filled diamond), 308.15 K (red filled square), 313.15 K (green filled triangle) and 318.15 K (purple filled circle). (Color figure online)

shrinkage of volume by hydrogen bonding of solvent molecules that take place on mixing of DMC and NMF molecules. Figure 3 represents the variation of excess partial molar volumes for DMC ($\bar{V}^E_{m,1}$) and NMF ($\bar{V}^E_{m,2}$) in the binary mixture with the mole fraction of DMC at *T* = (303.15, 308.15, 313.15, 318.15) K. Perusal of Fig. 3 shows that the values of $\bar{V}^E_{m,1}$ and $\bar{V}^E_{m,2}$ are negative at all temperatures which also indicate that the interaction is stronger between unlike molecules than like molecules [44]. Table 4 shows that $\bar{V}^{E,\infty}_{m,1}$ and $\bar{V}^{E,\infty}_{m,2}$ are negative, which further supports the conclusions drawn from the V_m^E data. Thus, lower values of $\bar{V}_{m,1}$, $\overline{V}_{m,2}$ and negative values of $\bar{V}^E_{m,1}$, $\bar{V}^E_{m,2}$, $\bar{V}^{E,\infty}_{m,1}$, $\bar{V}^{E,\infty}_{m,2}$ confirm the presence of strong interactions in the present binary system at all reported temperatures and support the V_m^E results.

Theoretical analysis: PFP theory

The Prigogine–Flory–Patterson (PFP) theory has been applied to predict and correlate excess molar volume. The relevant equations are given elsewhere [45–48]. This theory represents V_m^E by three contribution terms: the free volume, V_m^E(fv), the characteristic pressure, V_m^E(ip), and the energy of interaction, V_m^E(int). The Flory contact interaction parameter, χ_{12}, the only adjustable parameter, needed in the PFP theory was obtained by experimental V_m^E. The Flory contact interaction parameter, χ_{12}, was found to be negative for the investigated mixture at all temperatures. Table 5 reports the interaction parameter and calculated values of the three contributions from the PFP theory at mole fraction ≈ 0.5. The first contribution due to the interactional term V_m^E(int) representing the energy of interaction is negative for the system which is dominant and acts as a deciding factor for the sign and magnitude of excess molar volume due to its greater values compared to the other two contributions for the investigated system at all temperatures. Further, interaction parameter increases with temperature indicating the increase in strength of interaction with temperature. Thus, the variation of interaction parameter also supports the conclusions drawn from

Table 4 Partial molar volumes ($\bar{V}^{\infty}_{m,1}$, $\bar{V}^{\infty}_{m,2}$) and excess partial molar volumes ($\bar{V}^{E,\infty}_{m,1}$, $\bar{V}^{E,\infty}_{m,2}$) of the components at infinite dilution for binary mixture [dimethyl carbonate (1) + *N*-methylformamide (2)] at *T* = (303.15, 308.15, 313.15 and 318.15) K

T/K	$\bar{V}^{\infty}_{m,1}$/10^{-6} m^3 mol^{-1}	$\bar{V}^{E,\infty}_{m,2}$/10^{-6} m^3 mol^{-1}	$\bar{V}^{E,\infty}_{m,1}$/10^{-6} m^3 mol^{-1}	$\bar{V}^{\infty}_{m,2}$/10^{-6} m^3 mol^{-1}
303.15	83.5174	56.2669	− 1.7281	− 3.0635
308.15	83.1970	54.9328	− 2.5877	− 4.7037
313.15	82.5572	55.0358	− 3.7766	− 4.9051
318.15	82.8118	54.7186	− 4.0458	− 5.5494

Table 5 PFP interaction parameter, χ_{12}, and calculated values of the three contributions from the PFP theory at equimolar composition for (DMC + NMF) system at T = (303.15, 308.15, 313.15, 318.15) K

T/K	$\chi_{12}/10^6$ J m^{-3}	V_m^E(int)/10^{-6} m^3 mol^{-1}	V_m^E(fv)/10^{-6} m^3 mol^{-1}	V_m^E(ip)/10^{-6} m^3 mol^{-1}
303.15	− 101.291	− 0.7477	− 0.0370	− 0.0516
308.15	− 106.254	− 0.8627	− 0.0213	− 0.0650
313.15	− 143.151	− 0.9961	− 0.0097	− 0.0587
318.15	− 148.572	− 1.0279	− 0.0027	− 0.0383

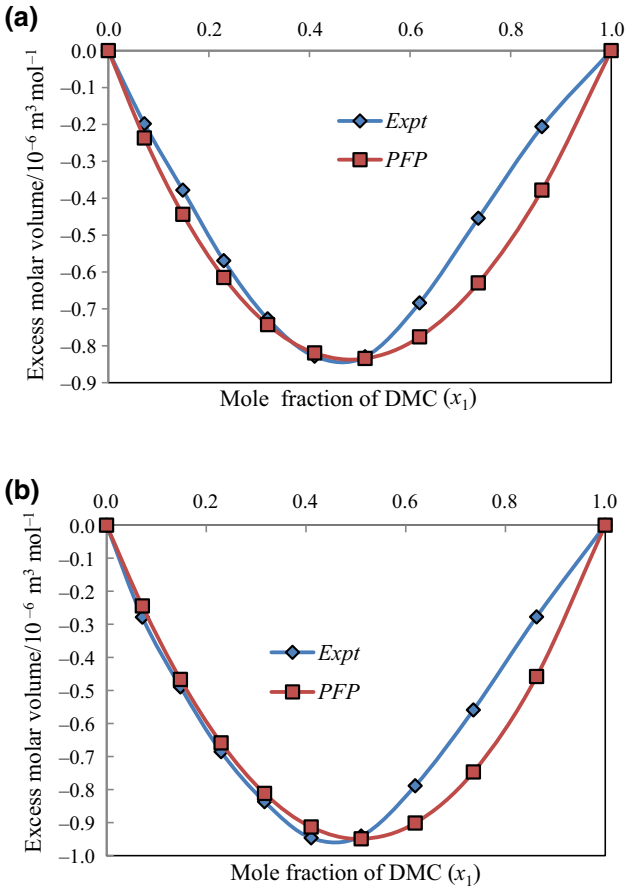

Fig. 4 Graph for V_m^E by experimental and PFP theory for binary system DMC + NMF at **a** 303.15 K and **b** 308.15 K

excess molar volume. Figure 4 shows the comparison between experimental and PFP theoretical excess molar volumes at 303.15 and 308.15 K. Similar trend is observed at other temperatures. Table 6 contains characteristic parameters for the pure components at several temperatures used in PFP theory calculations. It is evident from Fig. 4 that the PFP theory predicts the experimental data quite satisfactorily, while a small deviation in magnitude is observed for mole fraction > 0.5. We can conclude that it is possible to describe the volumetric behaviour of present mixture by the application of the PFP theory quite successfully.

Thermo-acoustic studies

Variation of excess isentropic compressibility (k_s^E) with mole fraction of DMC for the binary mixture of dimethyl carbonate and *N*-methylformamide at T = (303.15, 308.15, 313.15, 318.15) K is given in Table 7 and is graphically depicted in Fig. 5. According to Fort and Moore [49], a negative excess compressibility is an indication of strong hetero molecular interaction in the liquid mixtures, while a positive sign indicates weak interaction and is attributed to dispersion forces (London forces). Figure 5 illustrates that k_s^E values are negative over the entire mole fraction of DMC at all temperatures and absolute value of k_s^E increases linearly with increase in temperature. Negative sign in excess values of compressibility indicates that the mixture is less compressible than that of pure liquids which means molecules in the mixture are more effectively packed than

Table 6 Characteristic and reduced parameters for the pure components at T = (303.15, 308.15, 313.15, 318.15) K used in PFP theory

Component	T/K	$\hat{V}$	$P^*/10^6$ J mol^{-1}	$V^*/10^{-6}$ m^3 mol^{-1}	T^*/K
DMC	303.15	1.2638	796.4337	46.9460	5103.27
	308.15	1.2742	793.5125	46.8036	5060.21
	313.15	1.2845	810.6397	46.6632	5023.20
	318.15	1.2948	827.3969	46.2947	4992.66
NMF	303.15	1.3063	704.3887	65.2561	4646.91
	308.15	1.3063	685.4163	65.6686	4723.52
	313.15	1.3062	666.8093	66.0942	4801.15
	318.15	1.3061	649.1179	66.0998	4878.87

Table 7 Calculated excess isentropic compressibility (k_s^E), excess isothermal compressibility (k_T^E) and excess ultrasonic velocity (u^E) against mole fraction for binary mixture [dimethyl carbonate (1) + *N*-Methylformamide (2)] at T = (303.15, 308.15, 313.15 and 318.15) K

x_1	$k_s^E/10^{-10}$ pa^{-1}	$k_T^E/10^{-10}$ Pa^{-1}	u^E/m s^{-1}
303.15 K			
0.0000	0.0000	0.0000	0.0000
0.0718	− 0.1279	− 0.1679	14.8195
0.1482	− 0.2404	− 0.1915	26.6635
0.2297	− 0.3377	− 0.2525	35.5173
0.3169	− 0.4129	− 0.4605	41.3157
0.4104	− 0.4604	− 0.8193	43.9275
0.5107	− 0.4695	− 1.2220	42.9185
0.6189	− 0.4289	− 1.5214	37.9618
0.7357	− 0.3374	− 1.5879	29.0103
0.8623	− 0.1969	− 1.2397	16.4479
1.0000	0.0000	0.0000	0.0000
308.15 K			
0.0000	0.0000	0.0000	0.0000
0.0718	− 0.1507	− 0.1809	16.4056
0.1482	− 0.2794	− 0.2127	29.3823
0.2297	− 0.3865	− 0.2788	38.7651
0.3169	− 0.4690	− 0.4941	44.8732
0.4104	− 0.5228	− 0.8635	47.5770
0.5107	− 0.5340	− 1.2776	46.4921
0.6189	− 0.4906	− 1.5848	41.1525
0.7357	− 0.3920	− 1.6518	31.6381
0.8623	− 0.2311	− 1.2847	17.9472
1.0000	0.0000	0.0000	0.0000
313.15 K			
0.0000	0.0000	0.0000	0.0000
0.0718	− 0.1626	− 0.1876	16.8987
0.1482	− 0.3085	− 0.2282	30.5727
0.2297	− 0.4265	− 0.3007	40.3949
0.3169	− 0.5190	− 0.5248	46.7871
0.4104	− 0.5794	− 0.9054	49.6603
0.5107	− 0.5889	− 1.3274	48.3086
0.6189	− 0.5445	− 1.6435	42.9086
0.7357	− 0.4358	− 1.7083	32.9461
0.8623	− 0.2632	− 1.3284	18.9101
1.0000	0.0000	0.0000	0.0000
318.15 K			
0.0000	0.0000	0.0000	0.0000
0.0718	− 0.1820	− 0.1998	17.8029
0.1482	− 0.3416	− 0.2473	31.9664
0.2297	− 0.4731	− 0.3279	42.2790
0.3169	− 0.5748	− 0.5604	48.8490
0.4104	− 0.6368	− 0.9487	51.6183
0.5107	− 0.6471	− 1.3808	50.2371
0.6189	− 0.5986	− 1.7027	44.5029
0.7357	− 0.4865	− 1.7703	34.4966
0.8623	− 0.2925	− 1.3697	19.6607
1.0000	0.0000	0.0000	0.0000

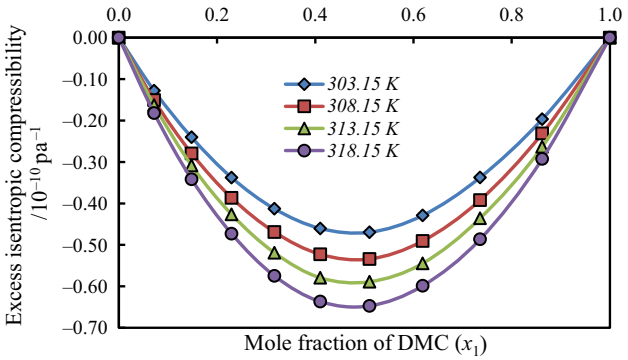

Fig. 5 Variation of excess isentropic compressibility (k_s^E) against mole fraction (x_1) of DMC for binary mixture [dimethyl carbonate (1) + *N*-methylformamide (2)] at T = 303.15 K (blue filled diamond), 308.15 K (red filled square), 313.15 K (green filled triangle) and 318.15 K (purple filled circle). (Color figure online)

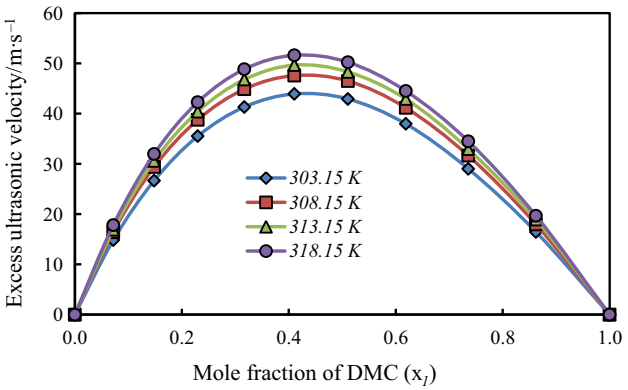

Fig. 6 Variation of excess ultrasonic velocity (u^E) against mole fraction (x_1) of DMC for binary mixture [dimethyl carbonate (1) + *N*-methylformamide (2)] at T = 303.15 K (blue filled diamond), 308.15 K (red filled square), 313.15 K (green filled triangle) and 318.15 K (purple filled circle). (Color figure online)

in their pure form. Thus, k_s^E also supports the occurrence of strong specific interaction in the binary mixture and the negative values of k_s^E increase with temperature, which suggest the increase in specific interactions with enhanced thermal energy of molecules [50]. Hence, values of k_s^E are observed to follow the trend: (318.15 > 313.15 > 308.15 > 303.15) K.

Table 8 Redlich–Kister coefficients of excess properties and corresponding standard deviations $\sigma(Y^E)$ for the binary system [dimethyl carbonate (1) + *N*-methylformamide (2)] at different temperatures

Property	*T*/K	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
$V_m^E/10^{-6}$ m^3 mol^{-1}	303.15	− 3.3078	− 1.1303	2.6697	0.4455	− 1.7455	0.0054
	308.15	− 3.7703	− 1.2367	2.5415	0.2503	− 2.5536	0.0097
	313.15	− 4.2775	− 1.4366	2.3913	1.0437	− 2.5222	0.0098
	318.15	− 4.7457	− 1.6301	1.9190	1.0454	− 2.3573	0.0128
$k_s^E/10^{-10}$ Pa^{-1}	303.15	− 1.8784	− 0.1881	0.2892	0.0295	− 0.2056	0.0006
	308.15	− 2.1362	− 0.1789	0.2523	− 0.0111	− 0.2775	0.0010
	313.15	− 2.3666	− 0.1989	0.2354	0.1132	− 0.2720	0.0018
	318.15	− 2.5974	− 0.2216	0.1583	0.1126	− 0.2432	0.0017
$k_T^E/10^{-10}$ pa^{-1}	303.15	− 4.7152	7.4598	0.3875	− 2.5214	− 5.3790	0.0039
	308.15	− 4.9318	7.6661	0.3147	− 2.6320	− 5.4383	0.0045
	313.15	− 5.1351	7.8455	0.2599	− 2.6309	− 5.4590	0.0046
	318.15	− 5.3414	8.0167	0.1722	− 2.7154	− 5.4711	0.0049
u^E/m s^{-1}	303.15	172.6711	49.2916	0.2063	3.2715	9.8073	0.0434
	308.15	186.8910	53.1211	4.9679	7.1962	10.4426	0.0626
	313.15	194.9110	56.2584	6.8636	1.8218	7.9856	0.1201
	318.15	202.2251	59.6721	11.8670	3.2057	5.7383	0.0709
$L_f^E/10^{-11}$ m	303.15	− 0.3803	− 0.0305	0.1082	0.0155	− 0.0708	0.0002
	308.15	− 0.4307	− 0.0244	0.0951	− 0.0015	− 0.0928	0.0003
	313.15	− 0.4771	− 0.0300	0.0884	0.0409	− 0.0843	0.0007
	318.15	− 0.5231	− 0.0375	0.0614	0.0382	− 0.0723	0.0006
$Z^E/10^6$ kg m^{-2} s^{-1}	303.15	0.1231	0.0422	− 0.0527	− 0.0148	0.0387	0.0001
	308.15	0.1320	0.0444	− 0.0474	− 0.0061	0.0536	0.0002
	313.15	0.1409	0.0497	− 0.0425	− 0.0237	0.0463	0.0003
	318.15	0.1490	0.0553	− 0.0295	− 0.0211	0.0400	0.0003

The variation of excess speed of sound, u^E, with the mole fraction of DMC at all temperatures is given in Table 7. From Fig. 6 u^E values are positive over the entire composition range and shows increase in its value as temperature is increased. Positive values of u^E are attributed to the increasing strength of interaction between component molecules of liquid mixture [51]. In binary mixtures, if the structure making effect is dominant which contributes to the formation of closely packed structure, sound waves will travel faster through the mixture and gives positive sign to the u^E. If structure breaking effect is dominant, speed of sound through the mixture will be slower and deviation will be negative. In the present study, positive values of u^E indicate the structure making effect [35, 52]. The trends of u^E with the temperature are opposite to those exhibited by k_s^E, and these are due to similar reasons as for k_s^E which further supports the behaviour of k_s^E with the temperature.

From Table 7, values of k_T^E show the similar trend like k_s^E at all the investigated temperatures. Negative values of k_T^E are attributed to the closer approach of unlike molecules [53] in the binary mixture, which reflects the existence of strong interaction between components of mixture at all temperatures.

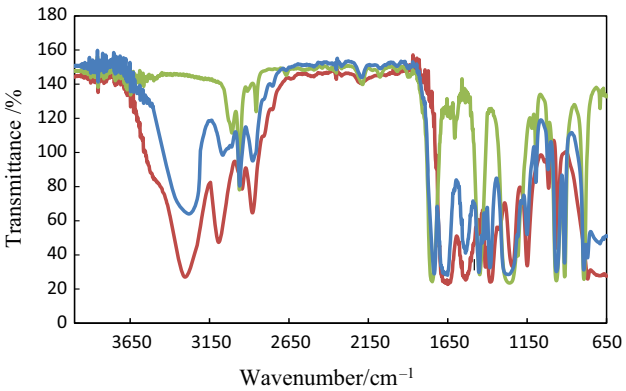

Fig. 7 Fourier-transform infrared spectra of liquid DMC (green), liquid NMF (red) and 1:1 liquid mixture of DMC + NMF (blue) at 298.15 K and atmospheric pressure. (Color figure online)

The existence of strong interactions between dimethyl carbonate and *N*-methylformamide is well supported by other derived excess parameters like intermolecular free length (L_f^E) and acoustic impedance (Z^E). Values of ultrasonic speed are correlated with certain semi-empirical relations of speed to test the applicability of various theories. Nonlinear parameter **(B/A)** along with certain molecular properties is also evaluated from the Sehgal's

Table 9 Neat FT-IR stretching frequencies of −NH and > C=O in pure components and their binary mixture of dimethyl carbonate (1) + *N*-methylformamide (2) at 298.15 K and P = 0.1 MPa

x_1	υ_{N-H}/cm^{-1}	$\upsilon_{c=o}$/cm^{-1} (DMC)	$\upsilon_{c=o}$/cm^{-1} (NMF)
0.0	3310	–	1681
0.2	3285	1750	1683
0.5	3280	1735	1684
0.7	3296	1749	1684
1.0	–	1756	–

equations which are kept in the supporting information file ***S***.

All the excess/deviation properties are correlated with Redlich–Kister polynomial equation to obtain their coefficients and standard deviation for the binary system (DMC + NMF) at all the investigated temperatures and are given in Table 8.

FT-IR studies

FT-IR spectroscopy has been extensively used to study intermolecular hydrogen bonding between component molecules in binary mixtures. FT-IR spectra of pure DMC, NMF and binary mixture are measured over the entire composition range and are reported for 1:1 composition in Fig. 7, and the data of frequencies of –NH and > C=O bands for certain compositions are listed in Table 9. In general, intermolecular hydrogen bonds give rise to broad bands, whereas bands arising from intra-molecular hydrogen bonds are sharp and well defined [54]. In dimethyl carbonate, C=O stretching band appears at 1756 cm^{-1} [55], C–H stretch of methyl group at 2960 cm^{-1}, C–O stretching at 1282 cm^{-1} and C–H deformation band at 1448 cm^{-1}. In NMF molecule, even nitrogen atom exhibits negative inductive effect; the greater mobility of lone pair of electrons present on nitrogen is involved in conjugation with the C=O group adjacent to it. Hence, C=O stretching band in NMF appears at lower wave number $\sim$ 1681 cm^{-1}. N–H stretching band in NMF appears at 3315 cm^{-1} [37]. Carbonyl group ($\sim$ 1681 cm^{-1}) in NMF can be differentiated from the carbonyl group ($\sim$ 1756 cm^{-1}) of DMC by its lower stretching frequency caused by resonance effect. By comparing the experimental FT-IR frequency values of binary mixtures with their respective pure components, we can get the information regarding type of intermolecular interaction present among the component liquids. Observing the FT-IR spectra (Fig. 7) for the equimolar binary mixture of system (dimethyl carbonate + *N*-methylformamide), there is a lower shift of 30 cm^{-1} wave number in the position of −NH and 19 cm^{-1} wave number in the position of C = O of DMC for the mixture compared with the pure spectrum of NMF and DMC. These shifts (towards lower wave number) are caused by the formation of strong intermolecular interactions like hydrogen bonding between the oxygen in carbonyl group of DMC and hydrogen in −NH group of NMF. However, the stretching vibrational frequency of C=O group of NMF in binary mixture does not change much, indicating that its contribution in the formation of hydrogen bond is negligible. From Table 9, we can notice that at equimolar composition υ_{N-H} band appears at lower frequency when compared to the other compositions. Thus, the study of FT-IR spectra shows the strength of complex formation maximum at $\sim$ 0.5 mol fraction of DMC for the DMC + NMF system at 298.15 K. In summary, the experimental results from thermo-acoustic and volumetric techniques have been well supported by FT-IR spectral analysis in the binary mixtures of DMC + NMF under investigation.

Conclusions

1. Density and speed of sound for the binary mixture [dimethyl carbonate (1) + *N*-methylformamide (2)] have been measured experimentally over the entire composition range at T = (303.15, 308.15, 313.15, 318.15) K.
2. To explore the nature of interaction in the present binary mixture, the experimental data have been used to compute the parameters like V_m^E, k_s^E, k_T^E, L_f^E, Z^E and u^E. The deviations/excess properties are fitted to Redlich–Kister-type polynomial equations. We observed positive values of Z^E and u^E and negative values of V_m^E, k_s^E, k_T^E, L_f^E for DMC + NMF mixture at all investigated temperatures, which clearly indicates the presence of specific interaction between unlike molecules. The strength of strong interaction with temperature is in the order: (318.15 > 315.15 > 308.15 > 303.15) K.
3. To know more about solute–solvent interaction, partial molar volume studies have been carried out. The observed lower values of $\bar{V}_{m,1}$, $\bar{V}_{m,2}$ and negative values of $\bar{V}_{m,1}^E$, $\bar{V}_{m,2}^E$, $\bar{V}_{m,1}^{E,\infty}$, $\bar{V}_{m,2}^{E,\infty}$ suggest volume contraction on mixing DMC with NMF. Further, the agreement between calculated and theoretical values by PFP is found to be good.
4. Nonlinear parameter (B/A) is evaluated using semi-empirical relations, and certain molecular properties are calculated from Sehgal's equations. Negative values of $(B/A)^E$ also support the existence of strong interaction between the components of mixture at all

temperatures. Furthermore, theoretical ultrasonic speeds in binary mixture are evaluated and validity of different theories is checked.

5. The results were analysed by FT-IR, in terms of molecular interactions through extensive hydrogen bonding among the component molecules in the binary liquid.

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