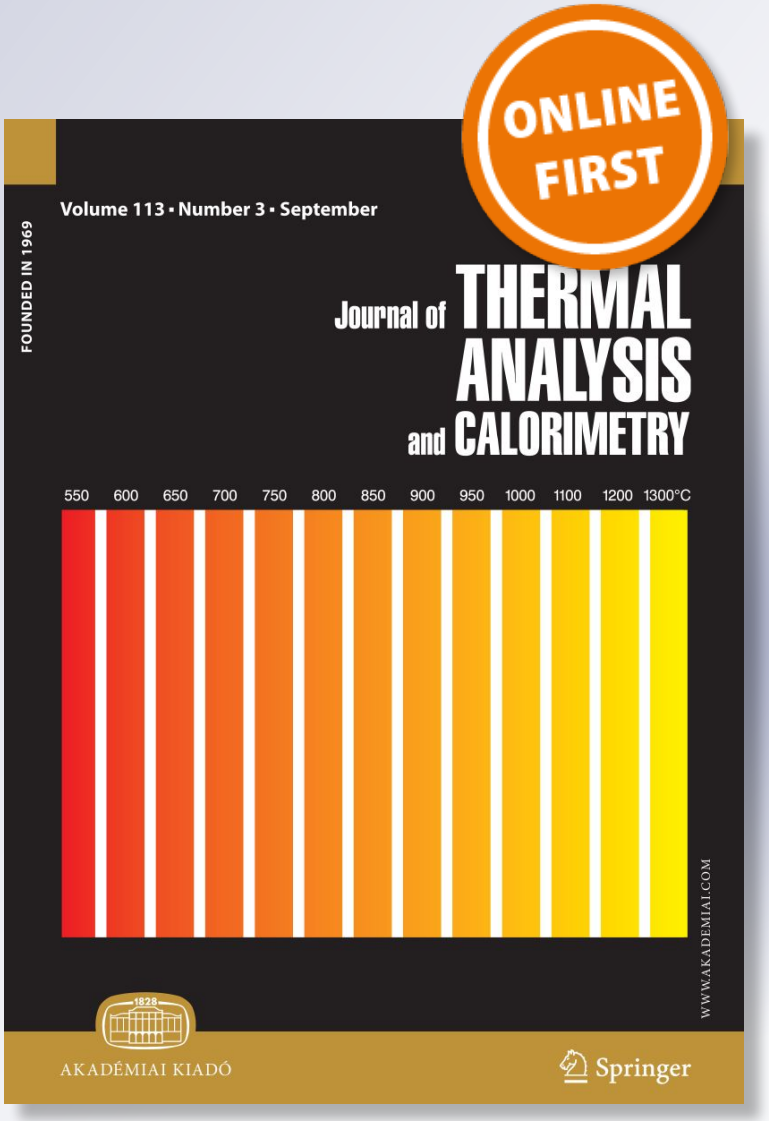
# *Steric and electronic effects to interpret non-covalent interactions in binary mixtures of dimethyl carbonate and isomeric cresols through thermophysical, acoustic and spectroscopic studies*

**Sk. Beebi, Sk. Md. Nayeem, P. B. Sandhya Sri, G. R. Satyanarayana, Zareena Begum & C. Rambabu**

**Journal of Thermal Analysis and Calorimetry**
An International Forum for Thermal Studies

ISSN 1388-6150

J Therm Anal Calorim
DOI 10.1007/s10973-017-6225-4




Springer

J Therm Anal Calorim
DOI 10.1007/s10973-017-6225-4

# Steric and electronic effects to interpret non-covalent interactions in binary mixtures of dimethyl carbonate and isomeric cresols through thermophysical, acoustic and spectroscopic studies

**Sk. Beebi[1,3] · Sk. Md. Nayeem[2] · P. B. Sandhya Sri[3] · G. R. Satyanarayana[4] · Zareena Begum[3] · C. Rambabu[3]**

Received: 30 October 2016 / Accepted: 18 February 2017


**Abstract** The densities ($\rho$), viscosities ($\eta$) and ultrasonic velocities ($u$) were measured for the binary mixtures of dimethyl carbonate (DMC) and isomeric cresols viz., *o*-cresol, *m*-cresol, *p*-cresol over the entire range of composition at atmospheric pressure and at different temperatures (303.15, 308.15,313.15, 318.15) K. From these experimental results, excess molar volume ($V_m^E$), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess intermolecular free length ($L_f^E$), excess acoustic Impedance ($Z^E$), deviation in viscosity ($\Delta\eta$), excess Gibbs free energy of activation of viscous flow ($\Delta G^{*E}$) and excess enthalpy ($H^E$) have been calculated. The excess or deviation properties were fitted to Redlich–Kister polynomial equation to obtain their coefficients and standard deviations. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions between the components of hetero molecules, and the nature of liquid mixtures has been discussed in terms of molecular interactions through steric and electronic effects. To know more about solute–solvent interactions, partial molar volumes ($\bar{V}_{m,1}, \bar{V}_{m,2}$) and excess partial molar volumes ($\bar{V}^E_{m,1}, \bar{V}^E_{m,2}$) have been computed. Further, variation of excess molar enthalpy with pressure is also evaluated to elucidate the molecular interactions in the liquid mixture. The present investigation also comprises of evaluation of the acoustic nonlinearity parameter ($B/A$) in the mixtures and calculation of cohesive energy ($\Delta A$), Van der Wall's constants ($a$, $b$), distance of closest approach ($d$). The FTIR provides support to the thermodynamic findings to explain specific interaction between unlike molecules.

**Keywords** Density · Ultrasonic velocity · Viscosity · Non-covalent interaction · FTIR analysis

## Introduction

Acoustic and thermodynamic properties derived from the density ($\rho$), viscosity ($\eta$), ultrasonic velocity ($u$) and FTIR spectral studies are useful to understand molecular behaviour in terms of various types of intermolecular interactions. The experimental data of excess thermodynamic properties of liquid mixtures provide knowledge about the type and magnitude of molecular interactions (non-covalent interactions) and can be used for the development of molecular models for describing the behaviour of solutions [1, 2]. Thermodynamic properties of binary liquids formed by mixing of two components associated through hydrogen bonds are interesting and important from both theoretical and process design aspects [3].

The selected components for the present study are dimethyl carbonate (DMC) and isomeric cresols viz., *o*-cresol (OC), *m*-cresol (MC) and *p*-cresol (PC). These have wide applicability in various chemical and pharmaceutical industries. Dimethyl carbonate is an environmentally benign and biodegradable chemical. Dialkyl carbonates have shown to be very useful in the lithium battery technology [4, 5] for the synthesis of many chemicals, as

✉ C. Rambabu
crbpublications@gmail.com

1 Department of Chemistry, Y.V.N.R. Govt. Degree College, Kaikaluru, AP 521333, India

2 Department of Physics, KRK Govt. Degree College, Addanki, AP 523201, India

3 Department of Chemistry, Acharya Nagarjuna University, Guntur, AP 522510, India

4 Department of Chemistry, Sir. C.R.Reddy College, Eluru, AP 534007, India

Published online: 14 March 2017

**Table 1** Comparison of density ($\rho$), viscosity ($\eta$) and ultrasonic velocity ($u$) of pure liquids with literature data at different temperatures

| Compound | $T$/K | $\rho/10^3$ kg m$^{-3}$ | | $\eta$/mPa s | | $u$/m s$^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | Expt. | Lit. | Expt. | Lit. | Expt. | Lit. |
| Dimethyl carbonate | 303.15 | 1.0567 | 1.056719[a] | 0.549 | 0.549[c] | 1176.0 | 1177[i] |
| | 308.15 | 1.0501 | 1.050071[a] | 0.518 | 0.517[c] | 1155.0 | 1153.7[j] |
| | 313.15 | 1.0434 | 1.043388[a] | 0.486 | 0.488[c] | 1135.0 | 1135[i] |
| | 318.15 | 1.0371 | 1.036687[a] | 0.473 | 0.472[d] | 1116.0 | – |
| *o*-cresol | 303.15 | 1.0362 | 1.0365[b] | 7.479 | – | 1485.3 | 1487[k] |
| | 308.15 | 1.0310 | 1.0313[b] | 5.963 | 5.5566[e] | 1466.7 | 1470[k] |
| | 313.15 | 1.0260 | 1.0263[b] | 4.238 | 4.243[f] | 1452.3 | 1452[l] |
| | 318.15 | 1.0211 | – | 2.215 | – | 1437.3 | 1441.8[m] |
| *m*-cresol | 303.15 | 1.0257 | 1.0264[b] | 8.929 | – | 1464.1 | 1465[k] |
| | 308.15 | 1.0215 | 1.0214[b] | 7.412 | 7.701[g] | 1449.5 | 1450[k] |
| | 313.15 | 1.0170 | 1.0163[b] | 6.116 | 6.120[g] | 1436.8 | 1435[l] |
| | 318.15 | 1.0135 | – | 5.019 | 5.022[g] | 1424.2 | 1426.4[m] |
| *p*-cresol | 303.15 | 1.0265 | 1.0262[b] | 9.539 | 10.070[h] | 1468.4 | 1471[k] |
| | 308.15 | 1.0220 | 1.0220[b] | 8.119 | 7.741[h] | 1455.8 | 1455[k] |
| | 313.15 | 1.0181 | 1.0180[b] | 6.741 | 6.661[f] | 1443.7 | 1439[l] |
| | 318.15 | 1.0139 | – | 5.469 | 5.292[h] | 1432.7 | 1431[m] |

[a] Ren et al. [18], [b] Sharma et al. [19], [c] Pereiro et al. [20], [d] Pal et al. [21], [e] Ahluwalia et al. [9], [f] Rosal et al. [22], [g] Yang et al. [23], [h] Umadevi et al. [24], [i] Rodrı'guez et al. [25], [j] Pardo et al. [26], [k] Bhatia et al. [27], [l] Siva kumar et al, [28], [m] Santhi et al. [29]

solvents for natural and synthetic resins and polymers. DMC is best used as a co-solvent for acrylics, urethane. Because of the good solvency, low toxicity and improved flash point for fire safety, DMC replaces methyl *tert*-butyl ether in fuels [6]. Phenols are widely used for the phonographic records, wood preservatives and selective weed killing [7]. Lysol and creosote are most widely known preparations with cresols (alkyl phenols). Both *ortho*- and *para*-cresols are used as end products in azo dyes [8].

The main purpose of this paper is to provide qualitative information for the characterisation of molecular interactions in the binary liquid mixtures of dimethyl carbonate and cresols. In this article, we report the values of excess molar volume ($V_m^E$), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess free length ($L_f^E$), excess acoustic impedance ($Z^E$), deviation in viscosity ($\Delta\eta$), excess Gibbs energy of activation for viscous flow ($\Delta G^{*E}$) and excess enthalpy ($H^E$) of DMC + isomeric cresols at four different temperatures. All the excess/deviation properties are fitted to Redlich–Kister-type equation, a multiparametric nonlinear regression analysis technique to derive the binary coefficients and to estimate the standard deviation between experimental and calculated data. In order to provide support to the $V_m^E$ values, partial molar volumes ($\bar{V}_{m,1}, \bar{V}_{m,2}$), excess partial molar volumes ($\bar{V}^E_{m,1}, \bar{V}^E_{m,2}$) have been computed. All the above parameters suggest the existence of molecular interactions between dimethyl carbonate and isomeric cresols giving stress on hydrogen bonding and steric effects. The infrared spectroscopic studies give further support to the existence of specific interactions through their change in bond-stretching vibrations.

The chemicals DMC and cresols (OC, MC, PC) have various applications in different fields; hence, an attempt has been made to study the molecular interaction between the binary systems (DMC + OC/MC/PC) at $T$ = (303.15, 308.15, 313.15 and 318.15) K. Many researchers have reported volumetric and viscometric studies of cresols in different binary mixtures [9–11]. The literature about binary liquid with one of the solvent as dimethyl carbonate is plenty [12–15]. A deep literature survey reveals that no significant work is available on the binary mixtures of dimethyl carbonate and isomeric cresols.

## Experimental

### Materials

DMC was obtained from Aldrich Chemical Co., with stated purity 99%. The chemicals *o*-, *m*- and *p*-cresols (S.D. Fine chemicals Ltd., India, mass fraction purity >0.99) are used in this study. All the chemicals were purified by the method described in the literature [16, 17]. Before the measurements, all the liquids were dried over molecular sieves (Union Carbide, type 4A) and stored in dark bottles. These

**Table 2** Ultrasonic velocities ($u$/m s$^{-1}$), densities ($\rho$/kg m$^{-3}$) and viscosities ($\eta$/mPa s) of binary mixtures of dimethyl carbonate with isomeric cresols at different temperatures $T$ = (303.15, 308.15, 313.15 and 318.15) K

| $x_1$ | 303.15 K | | | 308.15 K | | | 313.15 K | | | 318.15 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $u$/ m s$^{-1}$ | $\rho$/ $10^3$ kg m$^{-3}$ | $\eta$/ mPa s | $u$/ m s$^{-1}$ | $\rho$/ $10^3$ kg m$^{-3}$ | $\eta$/ mPa s | $u$/ m s$^{-1}$ | $\rho$/ $10^3$ kg m$^{-3}$ | $\eta$/ mPa s | $u$/ m s$^{-1}$ | $\rho$/ $10^3$ kg m$^{-3}$ | $\eta$/ mPa s |
| DMC + *o*-cresol | | | | | | | | | | | | |
| 0.0000 | 1485.3 | 1.0362 | 7.479 | 1466.7 | 1.0310 | 5.963 | 1452.3 | 1.0260 | 4.238 | 1437.3 | 1.0211 | 2.215 |
| 0.1197 | 1448.6 | 1.0387 | 6.115 | 1429.6 | 1.0334 | 4.915 | 1414.4 | 1.0285 | 3.533 | 1398.9 | 1.0236 | 1.905 |
| 0.2343 | 1413.4 | 1.0410 | 5.091 | 1394.1 | 1.0358 | 4.075 | 1378.2 | 1.0308 | 2.961 | 1362.2 | 1.0259 | 1.654 |
| 0.3441 | 1379.6 | 1.0433 | 4.216 | 1360.0 | 1.0381 | 3.351 | 1343.5 | 1.0329 | 2.461 | 1327.0 | 1.0279 | 1.442 |
| 0.4494 | 1347.2 | 1.0455 | 3.419 | 1327.3 | 1.0403 | 2.725 | 1310.2 | 1.0349 | 2.036 | 1293.3 | 1.0297 | 1.250 |
| 0.5504 | 1315.9 | 1.0475 | 2.729 | 1295.8 | 1.0421 | 2.201 | 1278.1 | 1.0365 | 1.661 | 1260.8 | 1.0312 | 1.075 |
| 0.6474 | 1285.8 | 1.0494 | 2.114 | 1265.5 | 1.0438 | 1.742 | 1247.2 | 1.0381 | 1.351 | 1229.5 | 1.0326 | 0.920 |
| 0.7407 | 1256.8 | 1.0511 | 1.618 | 1236.3 | 1.0454 | 1.351 | 1217.5 | 1.0395 | 1.078 | 1199.5 | 1.0339 | 0.786 |
| 0.8304 | 1228.9 | 1.0528 | 1.171 | 1208.2 | 1.0470 | 1.015 | 1189.0 | 1.0409 | 0.845 | 1170.6 | 1.0351 | 0.664 |
| 0.9168 | 1202.0 | 1.0547 | 0.798 | 1181.1 | 1.0486 | 0.731 | 1161.5 | 1.0422 | 0.641 | 1142.8 | 1.0362 | 0.562 |
| 1.0000 | 1176.0 | 1.0567 | 0.549 | 1155.0 | 1.0501 | 0.518 | 1135.0 | 1.0434 | 0.486 | 1116.0 | 1.0371 | 0.473 |
| DMC + *m*-cresol | | | | | | | | | | | | |
| 0.0000 | 1464.1 | 1.0257 | 8.929 | 1449.5 | 1.0215 | 7.412 | 1436.8 | 1.0170 | 6.116 | 1424.2 | 1.0135 | 5.019 |
| 0.1208 | 1429.7 | 1.0299 | 8.215 | 1414.2 | 1.0256 | 6.791 | 1400.5 | 1.0211 | 5.596 | 1387.1 | 1.0175 | 4.571 |
| 0.2362 | 1396.8 | 1.0340 | 7.415 | 1380.5 | 1.0294 | 6.159 | 1365.9 | 1.0248 | 5.102 | 1351.6 | 1.0211 | 4.171 |
| 0.3464 | 1365.2 | 1.0378 | 6.525 | 1348.2 | 1.0330 | 5.451 | 1332.7 | 1.0281 | 4.528 | 1317.7 | 1.0241 | 3.725 |
| 0.4519 | 1334.9 | 1.0411 | 5.645 | 1317.2 | 1.0362 | 4.715 | 1301.0 | 1.0311 | 3.945 | 1285.3 | 1.0268 | 3.264 |
| 0.5529 | 1305.7 | 1.0441 | 4.781 | 1287.4 | 1.0389 | 3.995 | 1270.5 | 1.0337 | 3.365 | 1254.1 | 1.0291 | 2.786 |
| 0.6498 | 1277.7 | 1.0468 | 3.899 | 1258.8 | 1.0414 | 3.256 | 1241.2 | 1.0359 | 2.751 | 1224.2 | 1.0311 | 2.298 |
| 0.7427 | 1250.8 | 1.0494 | 3.069 | 1231.2 | 1.0437 | 2.569 | 1213.0 | 1.0381 | 2.154 | 1195.5 | 1.0330 | 1.815 |
| 0.8319 | 1224.9 | 1.0518 | 2.235 | 1204.7 | 1.0458 | 1.874 | 1185.9 | 1.0400 | 1.561 | 1167.9 | 1.0346 | 1.315 |
| 0.9176 | 1199.9 | 1.0543 | 1.415 | 1179.3 | 1.0480 | 1.205 | 1159.9 | 1.0418 | 1.012 | 1141.4 | 1.0360 | 0.865 |
| 1.0000 | 1176.0 | 1.0567 | 0.549 | 1155.0 | 1.0501 | 0.518 | 1135.0 | 1.0434 | 0.486 | 1116.0 | 1.0371 | 0.473 |
| DMC + *p*-cresol | | | | | | | | | | | | |
| 0.0000 | 1468.4 | 1.0265 | 9.539 | 1455.8 | 1.0220 | 8.119 | 1443.7 | 1.0181 | 6.741 | 1432.7 | 1.0139 | 5.469 |
| 0.1207 | 1433.4 | 1.0301 | 8.561 | 1419.7 | 1.0255 | 7.265 | 1406.6 | 1.0215 | 6.012 | 1394.6 | 1.0174 | 4.886 |
| 0.2360 | 1399.9 | 1.0337 | 7.614 | 1385.2 | 1.0290 | 6.458 | 1371.2 | 1.0249 | 5.349 | 1358.2 | 1.0206 | 4.365 |
| 0.3463 | 1367.8 | 1.0371 | 6.651 | 1352.2 | 1.0324 | 5.661 | 1337.3 | 1.0279 | 4.705 | 1323.4 | 1.0234 | 3.850 |
| 0.4517 | 1337.0 | 1.0403 | 5.719 | 1320.5 | 1.0354 | 4.871 | 1304.8 | 1.0307 | 4.065 | 1290.1 | 1.0259 | 3.341 |
| 0.5527 | 1307.4 | 1.0433 | 4.789 | 1290.1 | 1.0381 | 4.084 | 1273.6 | 1.0331 | 3.415 | 1258.1 | 1.0282 | 2.796 |
| 0.6496 | 1279.0 | 1.0461 | 3.885 | 1260.9 | 1.0407 | 3.301 | 1243.6 | 1.0355 | 2.751 | 1227.3 | 1.0303 | 2.269 |
| 0.7425 | 1251.7 | 1.0487 | 3.015 | 1232.8 | 1.0431 | 2.549 | 1214.8 | 1.0377 | 2.135 | 1197.8 | 1.0323 | 1.764 |
| 0.8317 | 1225.5 | 1.0514 | 2.159 | 1205.8 | 1.0454 | 1.845 | 1187.1 | 1.0397 | 1.531 | 1169.4 | 1.0341 | 1.294 |
| 0.9175 | 1200.3 | 1.0540 | 1.329 | 1179.9 | 1.0478 | 1.157 | 1160.5 | 1.0417 | 0.976 | 1142.1 | 1.0357 | 0.859 |
| 1.0000 | 1176.0 | 1.0567 | 0.549 | 1155.0 | 1.0501 | 0.518 | 1135.0 | 1.0434 | 0.486 | 1116.0 | 1.0371 | 0.473 |

samples were distilled just before use. The chemicals after purification were 99.8% pure, and their purity was ascertained by GLC (gas liquid chromatography) and also by comparing experimental values of density, viscosity and ultrasound velocity at four different temperatures with those reported in the literature [18–29], as presented in Table 1.

## 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 stored in airtight bottles. The uncertainty on mole fraction

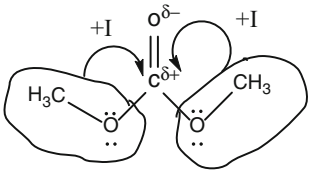



**Fig. 1** Polarity in dimethyl carbonate

is estimated to be $1 \times 10^{-4}$. The mixtures were preserved in well-stoppered conical flasks in order to minimise evaporation losses. After thorough mixing of liquids, the flasks were left undisturbed to attain thermal equilibrium.

The densities ($\rho$) 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 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 uncertainty in the measurement of density is found to be 2 parts in $10^4$ parts. The reproducibility in mole fractions was within $\pm 0.0002$.

Viscosities ($\eta$) of pure components and their binary mixtures are determined using a modified Ubbelohde suspended-level viscometer having 0.5 mm internal diameter of capillary curve. The method is based on the measurement of time in which constant volume of liquid passes through capillary of viscometer. The viscometer is suspended in a thermostatic water bath in which the temperature is maintained to $\pm 0.01$ K. At each temperature, the viscometer was calibrated against the known viscosities of benzene and carbon tetrachloride [30]. After the mixture had attained bath temperature, flow time has been measured. Five sets of readings for the flow time are taken with an electronic stopwatch with a precision of 0.01 s. Viscosity is estimated using the following formula:

$$\eta/\eta_w = \rho t/\rho_w t_w \quad (1)$$

The estimated uncertainty in the viscosity measurements is found to be <0.005 mPa s.

Temperature control for the measurement of viscosity and 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.

Ultrasonic velocities ($u$) in pure liquids and in their binary mixtures are measured using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, M-81 Model), working at a frequency of 2 MHz, calibrated with bi-distilled water, methanol and benzene at 298.15 K with an accuracy of $\pm 0.5$ m s$^{-1}$. The temperature was maintained by circulating water around the liquid cell from a U10 thermostat controlled to $\pm 0.01$ K.

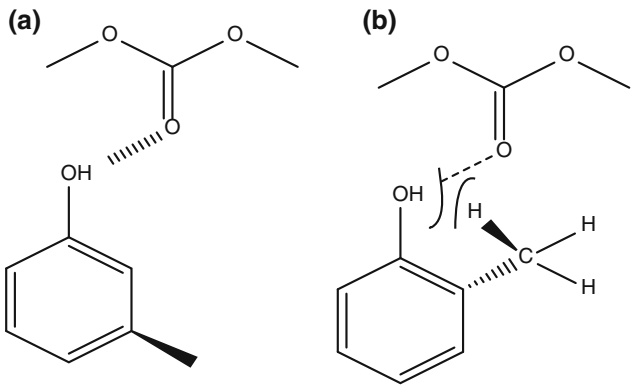



**Fig. 2** **a** Possible hetero-molecular hydrogen bonding in DMC + *m*-cresol binary system. **b** Steric effect domination over H-bonding among DMC + *o*-cresol system

## Theory

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

Molar volume ($V_m$) is evaluated with the equation

$$V_m = M_1 x_1 + M_2 x_2/\rho \quad (2)$$

Partial molar volume is an extensive property which depends on the phase composition at constant pressure and temperature. The partial molar volume of component $i$ in the binary mixtures, $\overline{V_i}$, is defined as

$$\overline{V_i} = (\partial V/\partial n_i)_{T,P,n_j} \quad (3)$$

where $n_i$ is the number of moles of the $i$th component added into the system and $n_j$ is the number of moles of the other components of the mixture. The partial molar volumes of components 1 and 2 $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ in the binary mixtures were calculated using the following equations:

$$\bar{V}_{m,1} = V_m^E + V_1^0 + (1 - x_1)\left(\partial V_m^E/\partial x_1\right)_{T,P} \quad (4)$$

$$\bar{V}_{m,2} = V_m^E + V_2^0 - x_1\left(\partial V_m^E/\partial x_1\right)_{T,P} \quad (5)$$

where $V_1^0$, $V_2^0$ are the molar volumes of dimethyl carbonate 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 volume of pure components are used to calculate the excess partial molar volumes using the equations:

**Table 3** Excess molar volume ($V_m^E$), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess intermolecular free length ($L_f^E$), excess acoustic impedance ($Z^E$) and deviation in viscosity ($\Delta\eta$) for the binary systems of DMC with isomeric cresols at temperatures $T$ = (303.15, 308.15, 313.15 and 318.15) K

| $x_1$ | $V_m^E$ /$10^{-6}$ $m^3$ $mol^{-1}$ | $\Delta\beta_{ad}$ /$10^{-12}m^2$ $N^{-1}$ | $L_f^E$ /$10^{-11}$ m | $Z^E$ /$10^{-3}$ kg $m^2$ $s^{-1}$ | $\Delta\eta$ /mPa s | $V_m^E$ /$10^{-6}$ $m^3$ $mol^{-1}$ | $\Delta\beta_{ad}$ /$10^{-12}m^2$ $N^{-1}$ | $L_f^E$ /$10^{-11}$ m | $Z^E$ /$10^{-3}$ kg $m^2$ $s^{-1}$ | $\Delta\eta$ /mPa s |
|---|---|---|---|---|---|---|---|---|---|---|
| DMC + OC | 303.15 K | | | | | 308.15 K | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1197 | −0.0391 | −0.1047 | 0.0001 | 1.0075 | −0.5340 | −0.0487 | −0.1110 | −0.0011 | 1.0229 | −0.3960 |
| 0.2343 | −0.0621 | −0.1771 | 0.0002 | 1.6630 | −0.7640 | −0.0960 | −0.1895 | −0.0020 | 1.9990 | −0.6120 |
| 0.3441 | −0.0841 | −0.2237 | 0.0001 | 2.1898 | −0.8780 | −0.1323 | −0.2401 | −0.0030 | 2.6883 | −0.7380 |
| 0.4494 | −0.1018 | −0.2448 | 0.0002 | 2.6386 | −0.9460 | −0.1500 | −0.2622 | −0.0031 | 3.0797 | −0.7910 |
| 0.5504 | −0.0946 | −0.2450 | 0.0002 | 2.4810 | −0.9360 | −0.1385 | −0.2602 | −0.0027 | 2.9049 | −0.7650 |
| 0.6474 | −0.0779 | −0.2250 | 0.0004 | 2.1291 | −0.8780 | −0.1209 | −0.2388 | −0.0022 | 2.5781 | −0.6960 |
| 0.7407 | −0.0451 | −0.1867 | 0.0010 | 1.4591 | −0.7280 | −0.0930 | −0.2001 | −0.0017 | 2.0118 | −0.5790 |
| 0.8304 | −0.0197 | −0.1346 | 0.0014 | 0.8879 | −0.5530 | −0.0640 | −0.1461 | −0.0011 | 1.4087 | −0.4260 |
| 0.9168 | −0.0069 | −0.0719 | 0.0010 | 0.4491 | −0.3280 | −0.0343 | −0.0795 | −0.0007 | 0.7356 | −0.2400 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| | 313.15 K | | | | | 318.15 K | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1197 | −0.0700 | −0.1221 | −0.0028 | 1.1860 | −0.2560 | −0.0869 | −0.1282 | −0.0036 | 1.3833 | −0.1010 |
| 0.2343 | −0.1238 | −0.2055 | −0.0043 | 2.1843 | −0.3980 | −0.1527 | −0.2164 | −0.0059 | 2.4901 | −0.1530 |
| 0.3441 | −0.1627 | −0.2572 | −0.0053 | 2.9151 | −0.4860 | −0.1912 | −0.2704 | −0.0071 | 3.1399 | −0.1740 |
| 0.4494 | −0.1797 | −0.2799 | −0.0054 | 3.2791 | −0.5160 | −0.2052 | −0.2923 | −0.0070 | 3.4767 | −0.1820 |
| 0.5504 | −0.1680 | −0.2785 | −0.0052 | 3.0662 | −0.5120 | −0.1941 | −0.2907 | −0.0068 | 3.2767 | −0.1810 |
| 0.6474 | −0.1451 | −0.2566 | −0.0049 | 2.6071 | −0.4580 | −0.1704 | −0.2684 | −0.0065 | 2.7996 | −0.1670 |
| 0.7407 | −0.1151 | −0.2157 | −0.0041 | 2.0393 | −0.3810 | −0.1384 | −0.2245 | −0.0052 | 2.2862 | −0.1390 |
| 0.8304 | −0.0837 | −0.1571 | −0.0028 | 1.5142 | −0.2770 | −0.1053 | −0.1652 | −0.0041 | 1.7006 | −0.1040 |
| 0.9168 | −0.0470 | −0.0853 | −0.0016 | 0.8360 | −0.1570 | −0.0605 | −0.0897 | −0.0023 | 0.9695 | −0.0560 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| DMC + MC | 303.15 K | | | | | 308.15 K | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1208 | −0.1113 | −0.1083 | −0.0026 | 2.0367 | 0.2980 | −0.1235 | −0.1175 | −0.0039 | 2.0797 | 0.2120 |
| 0.2362 | −0.1994 | −0.1841 | −0.0046 | 3.6709 | 0.4650 | −0.2162 | −0.1979 | −0.0064 | 3.7115 | 0.3750 |
| 0.3464 | −0.2667 | −0.2342 | −0.0066 | 4.8343 | 0.4990 | −0.2790 | −0.2481 | −0.0082 | 4.8078 | 0.4270 |
| 0.4519 | −0.2768 | −0.2526 | −0.0065 | 5.0939 | 0.5030 | −0.3003 | −0.2697 | −0.0088 | 5.1995 | 0.4180 |
| 0.5529 | −0.2585 | −0.2508 | −0.0064 | 4.7404 | 0.4860 | −0.2813 | −0.2663 | −0.0083 | 4.8886 | 0.3950 |
| 0.6498 | −0.2211 | −0.2283 | −0.0053 | 4.0973 | 0.4150 | −0.2408 | −0.2421 | −0.0070 | 4.2248 | 0.3230 |
| 0.7427 | −0.1681 | −0.1886 | −0.0038 | 3.1833 | 0.3630 | −0.1869 | −0.2035 | −0.0061 | 3.1943 | 0.2770 |
| 0.8319 | −0.1052 | −0.1355 | −0.0022 | 2.0487 | 0.2770 | −0.1212 | −0.1489 | −0.0045 | 1.9945 | 0.1970 |
| 0.9176 | −0.0589 | −0.0757 | −0.0018 | 1.0381 | 0.1750 | −0.0613 | −0.0813 | −0.0027 | 0.9419 | 0.1190 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| DMC + MC | 313.15 K | | | | | 318.15 K | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1208 | −0.1466 | −0.1292 | −0.0056 | 2.2743 | 0.1600 | −0.1622 | −0.1359 | −0.0064 | 2.4434 | 0.1020 |
| 0.2362 | −0.2474 | −0.2152 | −0.0088 | 3.9501 | 0.3160 | −0.2809 | −0.2314 | −0.0113 | 4.1852 | 0.2260 |
| 0.3464 | −0.3081 | −0.2690 | −0.0110 | 4.9118 | 0.3620 | −0.3406 | −0.2858 | −0.0134 | 5.1258 | 0.2810 |
| 0.4519 | −0.3322 | −0.2897 | −0.0113 | 5.4085 | 0.3730 | −0.3651 | −0.3075 | −0.0138 | 5.5941 | 0.3000 |

**Table 3** continued

| DMC + MC | 313.15 K | | | | | 318.15 K | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.5529 | −0.3158 | −0.2855 | −0.0107 | 5.1740 | 0.3620 | −0.3464 | −0.3040 | −0.0134 | 5.2730 | 0.2810 |
| 0.6498 | −0.2730 | −0.2597 | −0.0092 | 4.4901 | 0.2930 | −0.3099 | −0.2779 | −0.0121 | 4.6970 | 0.2330 |
| 0.7427 | −0.2255 | −0.2187 | −0.0081 | 3.6339 | 0.2190 | −0.2603 | −0.2330 | −0.0103 | 3.9141 | 0.1720 |
| 0.8319 | −0.1591 | −0.1607 | −0.0062 | 2.4848 | 0.1280 | −0.1894 | −0.1709 | −0.0078 | 2.7864 | 0.0780 |
| 0.9176 | −0.0874 | −0.0881 | −0.0038 | 1.2997 | 0.0620 | −0.1077 | −0.0938 | −0.0047 | 1.5259 | 0.0170 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| DMC + PC | 303.15 K | | | | | 308.15 K | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1207 | −0.0641 | −0.1054 | −0.0014 | 1.2456 | 0.1070 | −0.0735 | −0.1139 | −0.0022 | 1.3357 | 0.0640 |
| 0.2360 | −0.1112 | −0.1785 | −0.0024 | 2.1795 | 0.1970 | −0.1377 | −0.1946 | −0.0041 | 2.4875 | 0.1330 |
| 0.3463 | −0.1447 | −0.2246 | −0.0032 | 2.8238 | 0.2250 | −0.1837 | −0.2443 | −0.0053 | 3.3372 | 0.1740 |
| 0.4517 | −0.1637 | −0.2469 | −0.0038 | 3.1602 | 0.2410 | −0.2031 | −0.2677 | −0.0061 | 3.6612 | 0.1860 |
| 0.5527 | −0.1584 | −0.2466 | −0.0039 | 3.0301 | 0.2190 | −0.1876 | −0.2643 | −0.0055 | 3.4346 | 0.1660 |
| 0.6496 | −0.1316 | −0.2251 | −0.0032 | 2.5569 | 0.1860 | −0.1607 | −0.2415 | −0.0047 | 2.9726 | 0.1200 |
| 0.7425 | −0.0931 | −0.1870 | −0.0022 | 1.8553 | 0.1510 | −0.1241 | −0.2024 | −0.0039 | 2.2755 | 0.0740 |
| 0.8317 | −0.0582 | −0.1351 | −0.0012 | 1.2211 | 0.0970 | −0.0810 | −0.1478 | −0.0029 | 1.4609 | 0.0480 |
| 0.9175 | −0.0271 | −0.0719 | −0.0004 | 0.6153 | 0.0380 | −0.0417 | −0.0799 | −0.0016 | 0.7465 | 0.0120 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| | 313.15 | | | | | 318.15 | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1207 | −0.0923 | −0.1232 | −0.0033 | 1.5592 | 0.0260 | −0.1221 | −0.1345 | −0.0048 | 1.9299 | 0.0200 |
| 0.2360 | −0.1702 | −0.2090 | −0.0057 | 2.9133 | 0.0840 | −0.2033 | −0.2261 | −0.0078 | 3.2430 | 0.0750 |
| 0.3463 | −0.2132 | −0.2606 | −0.0070 | 3.6889 | 0.1300 | −0.2402 | −0.2790 | −0.0089 | 3.9117 | 0.1110 |
| 0.4517 | −0.2290 | −0.2832 | −0.0073 | 3.9936 | 0.1500 | −0.2599 | −0.3018 | −0.0091 | 4.3122 | 0.1290 |
| 0.5527 | −0.2181 | −0.2805 | −0.0070 | 3.8314 | 0.1310 | −0.2493 | −0.2987 | −0.0087 | 4.1596 | 0.0890 |
| 0.6496 | −0.1943 | −0.2580 | −0.0065 | 3.3766 | 0.0730 | −0.2239 | −0.2755 | −0.0083 | 3.6573 | 0.0450 |
| 0.7425 | −0.1609 | −0.2169 | −0.0057 | 2.7588 | 0.0380 | −0.1912 | −0.2316 | −0.0072 | 3.0940 | 0.0050 |
| 0.8317 | −0.1162 | −0.1597 | −0.0045 | 1.9273 | −0.0070 | −0.1373 | −0.1702 | −0.0056 | 2.1541 | −0.0200 |
| 0.9175 | −0.0681 | −0.0880 | −0.0030 | 1.0613 | −0.0260 | −0.0748 | −0.0937 | −0.0036 | 1.0823 | −0.0260 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

$$\bar{V}^{E}_{m,1} = \bar{V}_1 - V^0_1 \quad (6)$$

$$\bar{V}^{E}_{m,2} = \bar{V}_2 - V^0_2 \quad (7)$$

Adiabatic compressibility is given by the relation

$$\beta_{ad} = 1/\rho u^2 \quad (8)$$

The speed of sound ($u$) and the density of the medium ($\rho$) using Newton–Laplace equation give free length as follows

$$L_f = K_T/u\rho^{1/2} \quad (9)$$

where $K$ is the temperature-dependent Jacobson constant which is equal to $(93.875 + 0.375\ T) \times 10^{-8}$.

Acoustic impedance is given by

$$Z = u\rho \quad (10)$$

Further, Gibb's free energy of activation of viscous flow is given by

$$\Delta G^* = RT\left[\ln\left(\eta V_m\right)\right] \quad (11)$$

where $R$ is universal gas constant and $T$ is the absolute temperature.

Enthalpy $H$ is computed from $\pi_i$ and $V_m$ by using the relations of binary mixtures

$$H = \pi_i V_m \quad (12)$$

Excess/deviation properties such as $V^E_m, \Delta\beta_{ad}, L^E_f, Z^E, \Delta\eta, \Delta G^{*E}$ and $H^E$ have been calculated using the following equation:

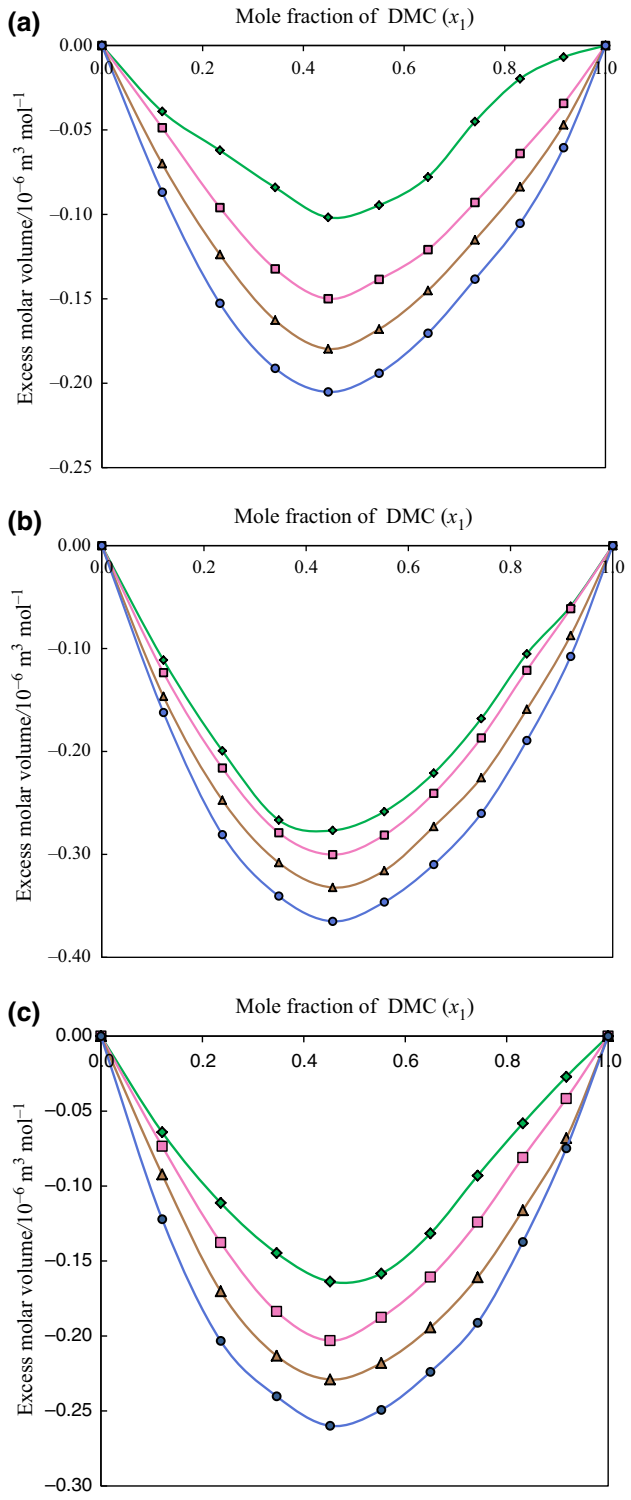



**Fig. 3** Variation of excess molar volume ($V_m^E/10^{-6}$ m$^3$ mol$^{-1}$) against mole fraction of DMC ($x_1$) for the binary systems **a** DMC(1) + *o*-cresol(2), **b** DMC(1) + *m*-cresol(2) and **c** DMC(1) + *p*-cresol(2) at (*filled diamond*) 303.15 K (*green line*) (*filled square*) 308.15 K (*pink line*), (*filled triangle*) 313.15 K (*brown line*) and (*filled circle*) 318.15 K (*blue line*). (Color figure online)

$$Y^{E} \quad \text{or } Y = Y_{mix} - (x_1 Y_1 + x_2 Y_2) \tag{13}$$

These excess or deviation properties were fitted to Redlich–Kister-type polynomial equation [31] by using the following formula

$$Y_{cal}^{E} = x_1 x_2 \sum_{i=1}^{n} A_{i-1}(x_2 - x_1)^{i-1} \tag{14}$$

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

$$\sigma = \left[\sum \left(Y_{expt}^{E} - Y_{cal}^{E}\right)^2 / (m-n)\right]^{1/2} \tag{15}$$

where $m$ is the number of experimental data points and $n$ is the number of coefficients considered, and $Y_{cal}^E$ have been obtained from the above Eqs. (13 and 14) using the best-fit values of $A_{i-1}$.

## Results and discussion

The experimental values of density ($\rho$), viscosity ($\eta$) and ultrasonic velocity ($u$) for binary mixtures (DMC + isomeric cresols) at temperatures (303.15, 308.15, 313.15 and 318.15) K are presented in Table 2. In all the three systems, it is observed that as the mole fraction of dimethyl carbonate increases the ultrasonic velocity and viscosity values decreases, whereas density values increases. This variation of ultrasonic velocity, viscosity and density of binary mixtures with the mole fraction ($x_1$) of dimethyl carbonate is observed at all the four different temperatures ranging from 303.15 to 318.15 K with an interval of 5 K. This nonlinear variation of density, viscosity and ultrasonic velocity with mole fraction of DMC indicates the presence of interaction between unlike molecules. The effect of interaction is well explained in terms of excess or deviation parameters which are found to be more sensitive towards intermolecular interactions in the liquid mixtures [32]. Any nonzero value in the excess parameter is a measure of nonlinearity and is the confirmation for the existence of interaction among the components of the systems [7].

As DMC posses hetero atom O (–C=O) and cresols have aromaticity along with the alcoholic –OH, there is a possibility of existence of significant degree of H-bonding between components of dimethyl carbonate and cresol (*ortho*/*meta*/*para*) binary mixtures. Dimethyl carbonate is a polar, aprotic solvent with a small dipole moment of 0.90 D. Because of the electro negativity difference between C

**Table 4** Partial molar volume of each component ($\bar{V}_{m,1}$, $\bar{V}_{m,2}$) calculated through partial molar volume Eqs. (4, 5) for dimethyl carbonate and isomeric cresols at four different temperatures

| $x_1$ | $\bar{V}_{m,1}/10^{-6}$ m$^3$ mol$^{-1}$ | | | | $\bar{V}_{m,2}/10^{-6}$ m$^3$ mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | DMC in OC | | | | OC in DMC | | | |
| | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| 0.0000 | 85.1384 | 85.3138 | 85.6263 | 85.4084 | 104.3620 | 104.8880 | 105.3990 | 105.9050 |
| 0.1197 | 85.1057 | 85.4304 | 85.9070 | 85.8198 | 104.3090 | 104.8820 | 105.3860 | 105.8840 |
| 0.2343 | 84.9820 | 85.4593 | 85.9549 | 86.0378 | 104.1570 | 104.8760 | 105.3760 | 105.8650 |
| 0.3441 | 84.9851 | 85.5001 | 85.9960 | 86.1668 | 103.9270 | 104.8590 | 105.3590 | 105.8450 |
| 0.4494 | 85.0769 | 85.5690 | 86.0734 | 86.2505 | 103.6600 | 104.8130 | 105.3070 | 105.7940 |
| 0.5504 | 85.1736 | 85.6501 | 86.1659 | 86.3051 | 103.4130 | 104.7310 | 105.2130 | 105.7000 |
| 0.6474 | 85.2266 | 85.7216 | 86.2456 | 86.3363 | 103.2380 | 104.6240 | 105.0950 | 105.5710 |
| 0.7407 | 85.2355 | 85.7692 | 86.2975 | 86.3481 | 103.1810 | 104.5170 | 104.9780 | 105.4300 |
| 0.8304 | 85.2289 | 85.7893 | 86.3229 | 86.3463 | 103.2610 | 104.4460 | 104.8870 | 105.3020 |
| 0.9168 | 85.2341 | 85.7894 | 86.3318 | 86.3386 | 103.4700 | 104.4520 | 104.8270 | 105.2000 |
| 1.0000 | 85.2460 | 85.7850 | 86.3340 | 86.3340 | 103.7640 | 104.5760 | 104.7740 | 105.1140 |
| | DMC in MC | | | | MC in DMC | | | |
| 0.0000 | 84.4824 | 85.0500 | 85.1342 | 84.8447 | 105.4300 | 105.8640 | 106.3310 | 106.6990 |
| 0.1208 | 84.5909 | 85.0408 | 85.4497 | 85.4001 | 105.3613 | 105.8639 | 106.3136 | 106.6718 |
| 0.2362 | 84.6398 | 85.0952 | 85.5990 | 85.7426 | 105.1825 | 105.8511 | 106.2816 | 106.6175 |
| 0.3464 | 84.7057 | 85.2055 | 85.7326 | 85.9527 | 104.9314 | 105.8045 | 106.2260 | 106.5507 |
| 0.4519 | 84.8118 | 85.3476 | 85.8789 | 86.0849 | 104.6443 | 105.7089 | 106.1278 | 106.4608 |
| 0.5529 | 84.9462 | 85.4938 | 86.0236 | 86.1729 | 104.3599 | 105.5603 | 105.9809 | 106.3268 |
| 0.6498 | 85.0801 | 85.6207 | 86.1468 | 86.2354 | 104.1210 | 105.3686 | 105.7947 | 106.1338 |
| 0.7427 | 85.1842 | 85.7127 | 86.2375 | 86.2806 | 103.9759 | 105.1582 | 105.5871 | 105.8854 |
| 0.8319 | 85.2410 | 85.7652 | 86.2950 | 86.3115 | 103.9791 | 104.9665 | 105.3754 | 105.6130 |
| 0.9176 | 85.2526 | 85.7839 | 86.3249 | 86.3288 | 104.1907 | 104.8426 | 105.1674 | 105.3808 |
| 1.0000 | 85.2460 | 85.7850 | 86.3340 | 86.3340 | 104.6760 | 104.8447 | 104.9543 | 105.2873 |
| | DMC in PC | | | | PC in DMC | | | |
| 0.0000 | 84.8529 | 85.2656 | 85.3553 | 85.3733 | 105.3530 | 105.8120 | 106.2170 | 106.6570 |
| 0.1207 | 84.9133 | 85.2963 | 85.7072 | 85.5867 | 105.2967 | 105.8103 | 106.1973 | 106.6441 |
| 0.2360 | 84.8364 | 85.3295 | 85.8518 | 85.7620 | 105.1344 | 105.8026 | 106.1672 | 106.6014 |
| 0.3463 | 84.8725 | 85.3961 | 85.9367 | 85.8981 | 104.8879 | 105.7744 | 106.1323 | 106.5393 |
| 0.4517 | 84.9938 | 85.4914 | 86.0212 | 86.0050 | 104.5990 | 105.7101 | 106.0755 | 106.4661 |
| 0.5527 | 85.1184 | 85.5956 | 86.1156 | 86.0931 | 104.3234 | 105.6042 | 105.9793 | 106.3783 |
| 0.6496 | 85.1958 | 85.6876 | 86.2077 | 86.1688 | 104.1183 | 105.4654 | 105.8397 | 106.2640 |
| 0.7425 | 85.2233 | 85.7520 | 86.2805 | 86.2338 | 104.0301 | 105.3186 | 105.6730 | 106.1116 |
| 0.8317 | 85.2272 | 85.7838 | 86.3230 | 86.2861 | 104.0839 | 105.2041 | 105.5183 | 105.9182 |
| 0.9175 | 85.2351 | 85.7889 | 86.3357 | 86.3212 | 104.2766 | 105.1758 | 105.4370 | 105.6972 |
| 1.0000 | 85.2460 | 85.7850 | 86.3340 | 86.3340 | 104.5727 | 105.2984 | 105.5108 | 105.4833 |

and O of carbonyl group in dimethyl carbonate, there arises partial negative charge on the oxygen atom ($O^{\delta-}$) and partial positive charge on the carbon atom ($C^{\delta+}$) of carbonyl group, thus it attains the polarity. Hence, there is a possibility of occurrence of dipole–dipole interaction in the dimethyl carbonate liquid. The partial positive charge on the carbon gets stabilised by the strong +I effect exhibited by the both -$OCH_3$ (strong electron donating) groups attached to the carbonyl group (C=O) of the dimethyl carbonate as shown in Fig. 1.

In cresols (methyl phenols), methyl group (–$CH_3$) is an $e^-$ directing in ortho- and para-positions, which increases

**Table 5** Excess partial molar volumes of each component ($\bar{V}^{E}_{m,1}$,$\bar{V}^{E}_{m,2}$) for the binary mixtures of dimethyl carbonate and isomeric cresols (ortho, meta and para) at four different temperatures

| $x_1$ | $\bar{V}^{E}_{m,1}/10^{-6}$ m$^3$ mol$^{-1}$ | | | | $\bar{V}^{E}_{m,2}/10^{-6}$ m$^3$ mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| DMC in OC | | | | | OC in DMC | | | |
| 0.0000 | −0.1080 | −0.4710 | −0.7080 | −0.9260 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1197 | −0.1400 | −0.3550 | −0.4270 | −0.5140 | −0.0530 | −0.0060 | −0.0130 | −0.0210 |
| 0.2343 | −0.2640 | −0.3260 | −0.3790 | −0.2960 | −0.2050 | −0.0120 | −0.0230 | −0.0400 |
| 0.3441 | −0.2610 | −0.2850 | −0.3380 | −0.1670 | −0.4350 | −0.0290 | −0.0400 | −0.0600 |
| 0.4494 | −0.1690 | −0.2160 | −0.2610 | −0.0830 | −0.7020 | −0.0750 | −0.0920 | −0.1110 |
| 0.5504 | −0.0720 | −0.1350 | −0.1680 | −0.0290 | −0.9490 | −0.1570 | −0.1860 | −0.2050 |
| 0.6474 | −0.0190 | −0.0630 | −0.0880 | 0.0020 | −1.1240 | −0.2640 | −0.3040 | −0.3340 |
| 0.7407 | −0.0100 | −0.0160 | −0.0360 | 0.0140 | −1.1810 | −0.3710 | −0.4210 | −0.4750 |
| 0.8304 | −0.0170 | 0.0040 | −0.0110 | 0.0120 | −1.1010 | −0.4420 | −0.5120 | −0.6030 |
| 0.9168 | −0.0120 | 0.0040 | −0.0020 | 0.0050 | −0.8920 | −0.4360 | −0.5720 | −0.7050 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | −0.5980 | −0.3120 | −0.6250 | −0.7910 |
| DMC in MC | | | | | MC in DMC | | | |
| 0.0000 | −0.7636 | −0.7350 | −1.1998 | −1.4893 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1208 | −0.6551 | −0.7442 | −0.8843 | −0.9339 | −0.0687 | −0.0001 | −0.0174 | −0.0272 |
| 0.2362 | −0.6062 | −0.6898 | −0.7350 | −0.5914 | −0.2475 | −0.0129 | −0.0494 | −0.0815 |
| 0.3464 | −0.5403 | −0.5795 | −0.6014 | −0.3813 | −0.4986 | −0.0595 | −0.1050 | −0.1483 |
| 0.4519 | −0.4342 | −0.4374 | −0.4551 | −0.2491 | −0.7857 | −0.1551 | −0.2032 | −0.2382 |
| 0.5529 | −0.2998 | −0.2912 | −0.3104 | −0.1611 | −1.0701 | −0.3037 | −0.3501 | −0.3722 |
| 0.6498 | −0.1659 | −0.1643 | −0.1872 | −0.0986 | −1.3090 | −0.4954 | −0.5363 | −0.5652 |
| 0.7427 | −0.0618 | −0.0723 | −0.0965 | −0.0534 | −1.4541 | −0.7058 | −0.7439 | −0.8136 |
| 0.8319 | −0.0050 | −0.0198 | −0.0390 | −0.0225 | −1.4509 | −0.8975 | −0.9556 | −1.0860 |
| 0.9176 | 0.0066 | −0.0011 | −0.0091 | −0.0052 | −1.2393 | −1.0214 | −1.1636 | −1.3182 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | −0.7540 | −1.0193 | −1.3767 | −1.4117 |
| DMC in PC | | | | | PC in DMC | | | |
| 0.0000 | −0.3931 | −0.5194 | −0.9787 | −0.9607 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1207 | −0.3327 | −0.4887 | −0.6268 | −0.7473 | −0.0563 | −0.0017 | −0.0197 | −0.0129 |
| 0.2360 | −0.4096 | −0.4555 | −0.4822 | −0.5720 | −0.2186 | −0.0094 | −0.0498 | −0.0556 |
| 0.3463 | −0.3735 | −0.3889 | −0.3973 | −0.4359 | −0.4651 | −0.0376 | −0.0847 | −0.1177 |
| 0.4517 | −0.2522 | −0.2936 | −0.3128 | −0.3290 | −0.7540 | −0.1019 | −0.1415 | −0.1909 |
| 0.5527 | −0.1276 | −0.1894 | −0.2184 | −0.2409 | −1.0296 | −0.2078 | −0.2377 | −0.2787 |
| 0.6496 | −0.0502 | −0.0974 | −0.1263 | −0.1652 | −1.2347 | −0.3466 | −0.3773 | −0.3930 |
| 0.7425 | −0.0227 | −0.0330 | −0.0535 | −0.1002 | −1.3229 | −0.4934 | −0.5440 | −0.5454 |
| 0.8317 | −0.0188 | −0.0012 | −0.0110 | −0.0479 | −1.2691 | −0.6079 | −0.6987 | −0.7388 |
| 0.9175 | −0.0109 | 0.0039 | 0.0017 | −0.0128 | −1.0764 | −0.6362 | −0.7800 | −0.9598 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | −0.7803 | −0.5136 | −0.7062 | −1.1737 |

e$^-$density in the –O–H bond thereby increasing basic nature of oxygen atom. Being strongly polarised O–H bond in cresols as $O^{\delta-}\cdots H^{\delta+}$, cresols are able to form strong hydrogen bonds in their pure state. Ali et al. [33] explained the formation of hydrogen bonding between DMSO and cyclohexanol molecules by excess acoustical studies. In the cresol (hydroxytoluene), para- and ortho-positions are more activated than meta-position, making the electron density high in these two positions than in the meta-position.

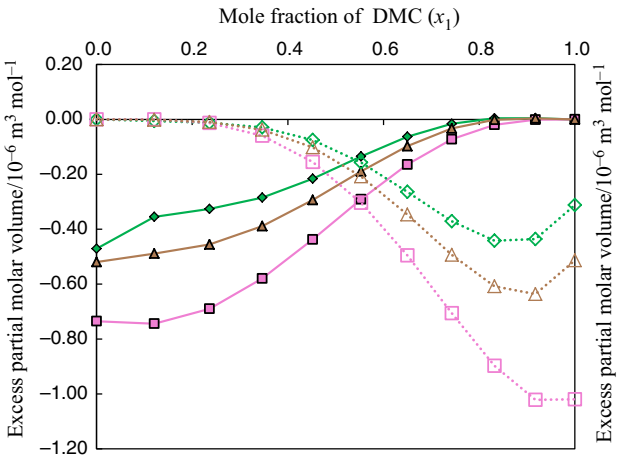
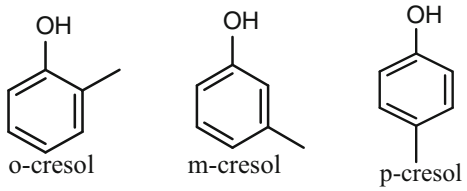



**Fig. 4** Variation of excess partial molar volume $\bar{V}^{E}_{m,1}$ of DMC (*solid line*) in OC (*filled diamond*), MC (*filled square*),PC (*filled triangle*) and $\bar{V}^{E}_{m,2}$ of OC (*diamond*), MC (*square*), PC (*triangle*) in DMC (*dotted line*) at 308.15 K against mole fraction ($x_1$) of DMC




The extent of interaction in isomeric cresols is explained by two effects: 1. electronic effect and 2. geometric effect. In *o*-cresol (OC), the closeness of –OH and $CH_3$ groups causes steric hindrance (geometric effect) which opposes close proximity of constituent molecules, and inductive effect increases the electron density in the O–H bond (electronic effect), which makes oxygen O of –OH group in cresols (*ortho* and *para*) more basic; thus, hydrogen atom of OH group in *o*-cresol is less available for the hetero-molecular hydrogen bond formation with oxygen atom of C=O group in DMC. These two effects decrease the strength of intermolecular hydrogen bond formation in *o*-cresol binary mixture than in *meta*- and *para*-cresols [29]. In *p*-cresol even there is no steric effect, inductive effect (Electronic effect) plays a role to decrease the strength of intermolecular hydrogen bond formation than in *m*-cresol (MC). In *m*-cresol, both steric and inductive effects diminish, thereby increasing the strength of interaction in DMC and *m*-cresol binary mixture. In the present study, we discuss various excess/deviation properties of binary mixtures which could explain strength of interaction among the component molecules. The schematic representation of the possible molecular interactions through the formation of hydrogen bonding is shown in Fig. 2.

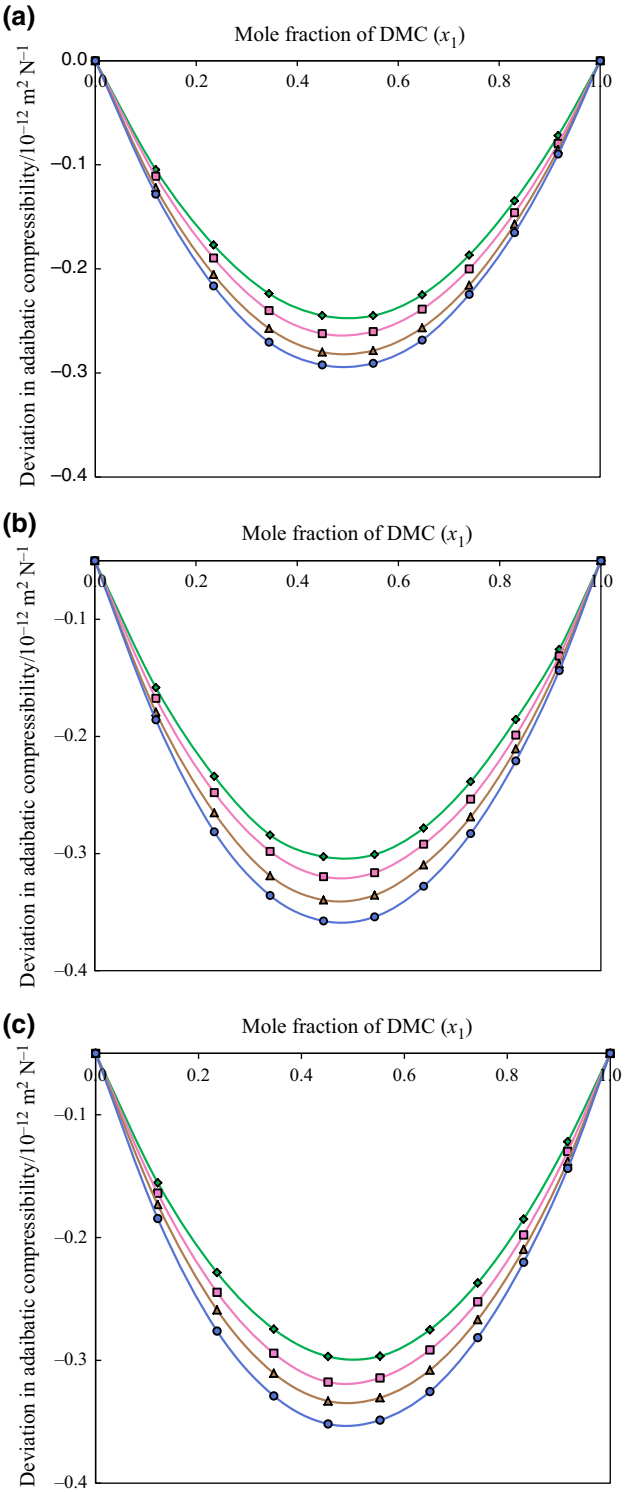



**Fig. 5** Plot of deviation in adiabatic compressibility ($\Delta\beta_{ad}$/$10^{-12}$m$^2$ N$^{-1}$) against mole fraction, $x_1$ of DMC for the systems **a** DMC(1) + *o*-cresol(2), **b** DMC(1) + *m*-cresol(2) and **c** DMC(1) + *p*-cresol(2) at (*filled diamond*) 303.15 K (*green line*), (*filled square*) 308.15 K (*pink line*), (*filled triangle*) 313.15 K (*brown line*), and (*filled circle*) 318.15 K (*blue line*). (Color figure online)

The values of excess/deviation parameters such as excess molar volumes, deviation in adiabatic compressibility, excess intermolecular free length, excess acoustic impedance and deviation in viscosity for various mole fractions of DMC $(x_1)$ and at four different temperatures for all the three binary mixtures are listed in Table 3.

Excess molar volume, $V_m^E$, is an important volumetric property by which molecular interactions between the component molecules in liquid mixtures can be assumed. The magnitude and the sign of $V_m^E$ can be qualitatively examined by considering the physical, structural and chemical contributions [34]. The extent/degree of volume compression or volume expansion decides the magnitude and sign of the $V_m^E$ Negative excess molar volumes indicate possibility of dominance/existence of strong interactions between unlike molecules in the liquid mixture [35], whereas positive values indicate predominance of dispersion forces between the molecules in the mixture [19]. The variation of excess molar volume ($V_m^E$) with mole fraction of dimethyl carbonate at four different temperatures (303.15–318.15 K) is shown in Fig. 3a–c for all the systems. The excess molar volume is considered as the resultant contribution from several opposing effects such as chemical, physical and structural [36].

The factors that are responsible for negative excess molar volumes are:

i. Physical contribution: Association through weak physical forces such as Van der Wall forces, dipolar forces, dipole-induced dipole interactions.
ii. Structural contribution: Difference in molar volumes and free volumes between liquid components, geometry of molecular structure, which favours fitting of the component molecules within the voids of each other.
iii. Chemical contribution: Chemical interaction among component molecules in the form of hetero-molecular association through H-bonding.

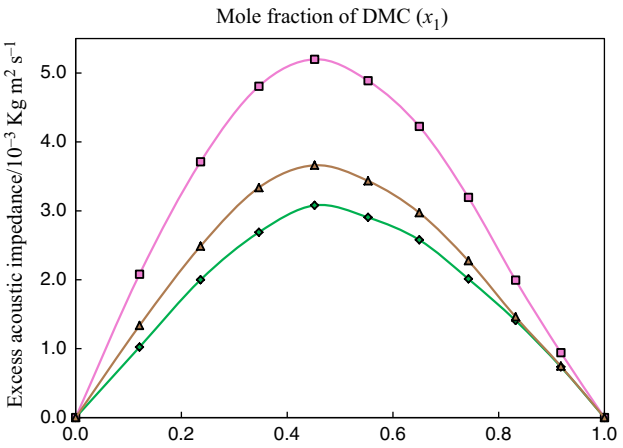



**Fig. 7** Variation of excess acoustic impedance ($Z^E/10^{-3}$ kg m$^2$ s$^{-1}$) against mole fraction, $x_1$ of DMC for the binary systems of DMC with OC (*filled diamond*) (*green line*), MC (*filled square*) (*pink line*) and PC (*filled triangle*) (*brown line*) at 308.15 K. (Color figure online)

The factors that are responsible for positive excess molar volumes are:

i. Physical contribution: Breaking up of associates held together by weaker physical forces such as dipole–dipole or dipole-induced dipole interactions or by any other Van der Waals forces.
ii. Structural contribution: Steric hindrance which opposes the close proximity of the constituent

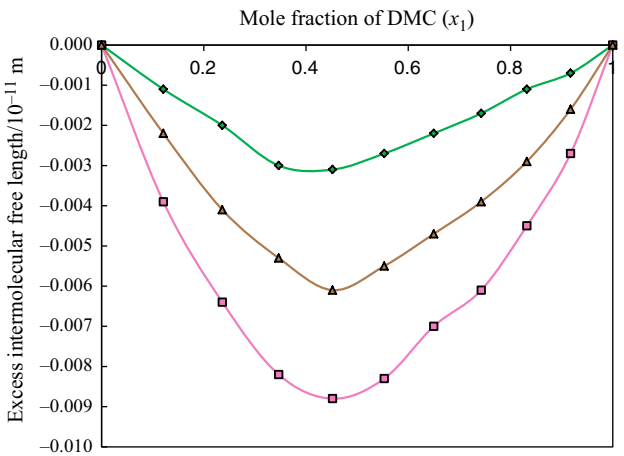



**Fig. 6** Plot of excess intermolecular free length ($L_f^E/10^{-11}$ m) against mole fraction, $x_1$ of DMC for the binary systems of DMC with OC (*filled diamond*) (*green line*), MC (*filled square*) (*pink line*) and PC (*filled triangle*) (*brown line*) at 308.15 K. (Color figure online)

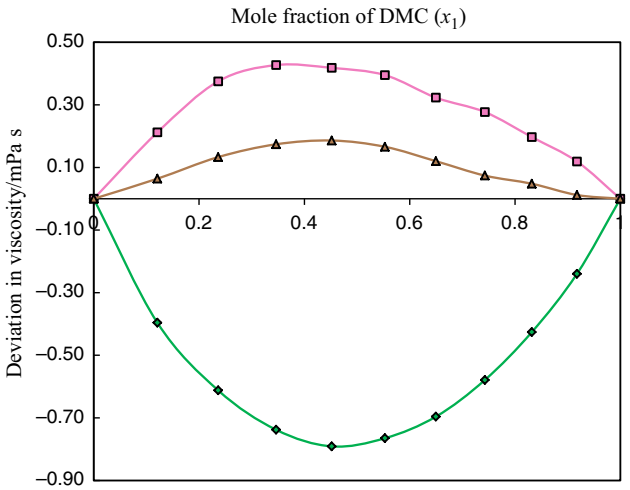



**Fig. 8** Plot of deviation in viscosity ($\Delta\eta$/mPa s) against mole fraction, $x_1$ of DMC for the binary systems of DMC with OC (*filled diamond*) (*green line*), MC (*filled square*) (*pink line*) and PC (*filled triangle*) (*brown line*) at 308.15 K. (Color figure online)

**Table 6** Excess values of Gibbs free energy of activation for viscous flow ($\Delta G^{*E}$) and enthalpy ($H^E$) of DMC + cresols (OC/MC/PC) at four different temperatures

| $x_1$ | $\Delta G^{*E}$/J mol$^{-1}$ | | | | $H^E$/J mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| DMC + OC | | | | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1197 | 284.8790 | 258.4818 | 204.8542 | 93.1805 | 0.0386 | 0.0963 | 0.0249 | -0.1373 |
| 0.2343 | 580.4939 | 498.2019 | 393.5131 | 189.4911 | 1.2054 | 0.6663 | 0.3978 | 0.0295 |
| 0.3441 | 829.7158 | 685.7286 | 532.3424 | 276.3823 | 2.3082 | 1.1094 | 0.6134 | 0.3220 |
| 0.4494 | 995.2849 | 815.5930 | 633.0110 | 329.1063 | 2.7889 | 1.3814 | 0.8427 | 0.4793 |
| 0.5504 | 1092.4531 | 901.2215 | 672.9978 | 343.0809 | 3.0260 | 1.7074 | 0.8454 | 0.4799 |
| 0.6474 | 1087.1320 | 908.9577 | 681.9507 | 327.1894 | 2.7007 | 1.7214 | 0.9839 | 0.4202 |
| 0.7407 | 1026.2479 | 840.4895 | 619.0956 | 290.7295 | 2.5584 | 1.5674 | 0.8756 | 0.3799 |
| 0.8304 | 799.9834 | 667.6318 | 489.1389 | 209.2099 | 1.5956 | 1.1105 | 0.6539 | 0.1814 |
| 0.9168 | 398.8893 | 364.7662 | 254.3525 | 118.6128 | 0.2105 | 0.3556 | 0.1278 | 0.1002 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| DMC + MC | | | | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1208 | 642.2069 | 602.0607 | 567.2665 | 509.2478 | 6.9408 | 6.0336 | 5.3167 | 4.4075 |
| 0.2362 | 1196.7153 | 1139.8951 | 1088.6744 | 988.5684 | 12.4281 | 11.1940 | 10.1526 | 8.6366 |
| 0.3464 | 1650.3223 | 1579.5973 | 1505.8292 | 1379.1301 | 16.2863 | 14.8694 | 13.4850 | 11.7130 |
| 0.4519 | 2027.6403 | 1927.7384 | 1843.0272 | 1689.1575 | 19.1607 | 17.3239 | 15.8577 | 13.8627 |
| 0.5529 | 2319.5442 | 2192.3734 | 2095.4846 | 1901.8656 | 21.0124 | 18.8546 | 17.3137 | 14.9540 |
| 0.6498 | 2486.1364 | 2328.4586 | 2209.4757 | 1997.3216 | 21.3421 | 18.9220 | 17.2281 | 14.8935 |
| 0.7427 | 2535.2163 | 2354.0256 | 2184.2940 | 1952.8550 | 20.6444 | 18.1428 | 15.9675 | 13.6760 |
| 0.8319 | 2361.7563 | 2152.8364 | 1932.9818 | 1656.7830 | 17.9055 | 15.4042 | 12.9671 | 10.5215 |
| 0.9176 | 1809.6863 | 1603.7527 | 1368.0574 | 1082.9634 | 12.4484 | 10.4323 | 8.2865 | 6.1207 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| DMC + PC | | | | | | | | |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1207 | 600.2996 | 570.3914 | 531.9986 | 486.0931 | 5.8749 | 5.2156 | 4.4819 | 3.8756 |
| 0.2360 | 1137.4231 | 1084.0871 | 1019.2280 | 936.2518 | 10.9215 | 9.7934 | 8.5966 | 7.5350 |
| 0.3463 | 1591.5064 | 1525.1456 | 1441.3105 | 1319.3564 | 14.7652 | 13.4431 | 11.9732 | 10.4519 |
| 0.4517 | 1970.7272 | 1884.4409 | 1783.5684 | 1627.8199 | 17.6923 | 16.0841 | 14.4233 | 12.5738 |
| 0.5527 | 2250.5620 | 2145.6709 | 2021.9110 | 1811.1429 | 19.3701 | 17.5682 | 15.6857 | 13.2733 |
| 0.6496 | 2419.8830 | 2282.8549 | 2121.6653 | 1885.3837 | 19.8492 | 17.7141 | 15.4888 | 13.0389 |
| 0.7425 | 2448.6137 | 2274.6709 | 2096.7967 | 1819.9872 | 18.9968 | 16.5832 | 14.3991 | 11.7555 |
| 0.8317 | 2247.0917 | 2074.0327 | 1840.3198 | 1576.8012 | 16.1472 | 14.0902 | 11.5829 | 9.4159 |
| 0.9175 | 1638.4112 | 1480.5331 | 1253.0179 | 1046.4140 | 10.5155 | 9.0214 | 7.0411 | 5.6401 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

molecules and geometry of the molecular structure which does not favour fitting of the component molecules into the voids of each other.

iii. Chemical contribution: Rupture of association like H-bonding by the addition of one of the component molecules to the other during the mixing process.

The graphical representation in Fig. 3a–c and values from Table 3 show variation of excess molar volume with mole fraction ($x_1$) of DMC for all the binary mixtures and at different temperatures. At 303.15 K, excess molar volume for binary mixtures is as follows: For DMC + *o*-cresol $V_m^E = -0.1018 \times 10^{-6}$ m$^3$ mol$^{-1}$ at $x_1 = 0.4494$,

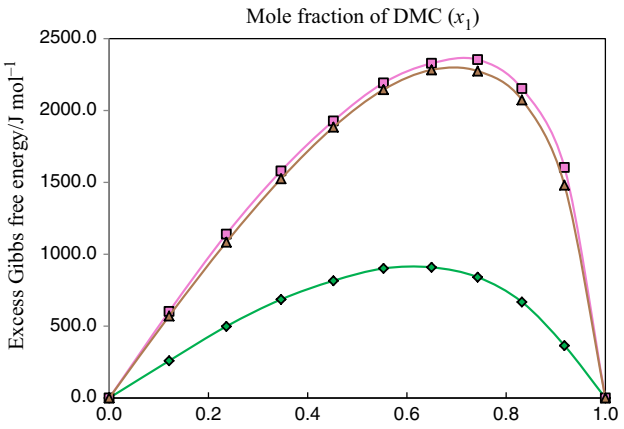



**Fig. 9** Plot of excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$/J mol$^{-1}$) against the mole fraction, $x_1$ of DMC for the binary mixtures of DMC with OC (*filled diamond*) (*green line*), MC (*filled square*) (*pink line*) and PC (*filled triangle*) (*brown line*) at 308.15 K. (Color figure online)

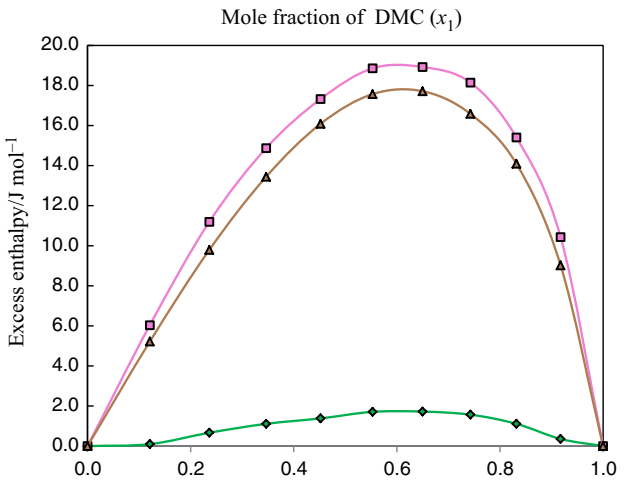



**Fig. 10** Plot of variation of excess enthalpy ($H^E$/J mol$^{-1}$) with the mole fraction, $x_1$ of DMC for the binary mixtures of DMC with OC (*filled diamond*) (*green line*), MC (*filled square*) (*pink line*) and PC (*filled triangle*) (*brown line*) at 308.15 K. (Color figure online)

for DMC + *m*-cresol $V_m^E = -0.2768 \times 10^{-6}$ m$^3$ mol$^{-1}$ at $x_1 = 0.4519$ and for DMC + *p*-cresol $V_m^E = -0.1637 \times 10^{-6}$ m$^3$ mol$^{-1}$ at $x_1 = 0.4517$. The same type of trend can also be observed for other temperatures. In other words, the order of magnitude of $V_m^E$ of DMC (1) + *o*-cresol (2), + *m*-cresol (2), + *p*-cresol (2) at minima is as follows: *m*-cresol > *p*-cresol > *o*-cresol. The observed higher negative values of $V_m^E$ for DMC + *m*-cresol binaries over the entire range of mole fraction may be attributed to the dominance of molecular association (more contraction of volume in *m*-cresol binary mixture). Further, the results shown in Fig. 3 reveal that for the binary liquid mixtures of dimethyl carbonate with isomeric cresols {DMC(1) + OC(2), + MC(2), + PC(2)}, excess molar volumes are negative for all the systems over the entire range of composition. Furthermore, the negative excess molar volume,$V_m^E$, indicate volume contraction on mixing. This fact suggests formation of hetero-molecular hydrogen bonding among DMC and cresol molecules and is also due to the favourable fitting of small-sized molecules into the voids created by large molecules [the molar volumes of pure components of DMC, OC, MC, PC are (85.246, 104.262, 105.430, 105.353) $\times 10^{-6}$ m$^3$ mol$^{-1}$, respectively, at 303.15 K], which favours fitting of the component molecules within the voids of each other resulting in negative $V_m^E$ values [37]. $V_m^E$ are less negative for system DMC + OC than other system suggesting that the strength of the hydrogen bond formed should follow the order: *m*-cresol > *p*-cresol > *o*-cresol. This may be convincingly explained by considering DMC as a proton acceptor, which forms hydrogen bond more favourably with *m*-cresol (a good proton donor) as compared to other cresols.

Therefore, the observed negative values of $V_m^E$ and the order of strength of strong interactions are due to cumulative effect of all the above-mentioned factors. In short, the dominance of prevailing strong interactions over the dispersion (physical) makes the molecules of the binary liquid move closer leading to the observed negative values of $V_m^E$. Thus, the order of strong interaction among the binaries is: (DMC +MC) > (DMC + PC) > (DMC + OC). Moreover, with increase in temperature, the magnitude of negative $V_m^E$ value increases for all the three binary mixtures, which further explains strengthening of molecular interaction with increase in temperature. The order of strength of interaction thus follows: (318.15 > 313.15 > 308.15 > 303.15) K.

Partial molar volume is an extensive property of a liquid (solution/mixture) which changes with change in number of moles of a component of liquid mixture. Partial molar volume of a substance *i* in a mixture is given as change in volume per mole of *i* added to the mixture. The changing molecular environment decides the thermodynamic properties of a mixture as its composition is altered. To understand the molecular interaction in binary liquid mixtures, partial molar volume $\bar{V}_m$ studies have been adopted. Partial molar volumes of DMC in cresols (*ortho*, *meta* and *para*) ($\bar{V}_{m,1}$) and cresols (*ortho*, *meta* and *para*) in DMC ($\overline{V}_{m,2}$) have been derived by Eqs. (4, 5). The values of partial molar volumes of component 1 and 2 at four different temperatures over entire mole fraction range are tabulated in Table 4. From this table, 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 contraction of volume take place on mixing of DMC to the cresol molecules [37]. Excess partial molar volumes for DMC in cresols ($\bar{V}_{m,1}^E$) and cresols in DMC ($\bar{V}_{m,2}^E$) are given in Table 5. Perusal of

**Table 7** Redlich–Kister coefficients $A_{i-1}$ and corresponding standard deviations ($\sigma$) computed for excess/deviation properties of the binary mixtures of DMC and isomeric cresols (ortho, meta and para) at different temperatures

| Property | Temp/K | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| Dimethyl carbonate(1) + *o*−cresol(2) | | | | | | | |
| $V_m^E/10^{-6}$ m$^3$ mol$^{-1}$ | 303.15 | −0.3958 | −0.0744 | 0.5832 | −0.1709 | −0.5402 | 0.0023 |
| | 308.15 | −0.5748 | −0.1287 | 0.2364 | 0.2084 | −0.0530 | 0.0025 |
| | 313.15 | −0.6973 | −0.1614 | 0.2318 | 0.2026 | −0.2010 | 0.0019 |
| | 318.15 | −0.8050 | −0.1949 | 0.1277 | 0.2623 | −0.1808 | 0.0012 |
| $\Delta\beta_{ad}/10^{-12}$ m$^2$ N$^{-1}$ | 303.15 | −0.9916 | −0.0114 | 0.0525 | −0.0297 | −0.0301 | 0.0005 |
| | 308.15 | −1.0550 | −0.0340 | 0.0049 | 0.0446 | 0.0146 | 0.0006 |
| | 313.15 | −1.1276 | −0.0268 | −0.0423 | 0.0034 | 0.0379 | 0.0006 |
| | 318.15 | −1.1794 | −0.0503 | −0.0479 | 0.0388 | 0.0360 | 0.0008 |
| $L_f^E/10^{-11}$ m | 303.15 | 0.0003 | −0.0028 | 0.0132 | −0.0082 | 0.0066 | 0.0001 |
| | 308.15 | −0.0117 | −0.0068 | 0.0020 | 0.0104 | 0.0024 | 0.0001 |
| | 313.15 | −0.0214 | −0.0038 | −0.0102 | 0.0012 | 0.0096 | 0.0001 |
| | 318.15 | −0.0282 | −0.0088 | −0.0110 | 0.0103 | 0.0080 | 0.0002 |
| $\Delta\eta$/mPa s | 303.15 | −3.792 | −0.109 | −0.172 | −0.903 | −2.075 | 0.009 |
| | 308.15 | −3.126 | −0.365 | −0.221 | −0.128 | −0.507 | 0.004 |
| | 313.15 | −2.091 | −0.207 | 0.117 | −0.113 | −0.592 | 0.003 |
| | 318.15 | −0.736 | −0.057 | −0.113 | −0.163 | −0.126 | 0.002 |
| $Z^E/10^{-3}$ kg m$^2$ s$^{-1}$ | 303.15 | 10.2400 | 1.0352 | −10.6513 | 2.3561 | 10.9269 | 0.0545 |
| | 308.15 | 11.9436 | 1.5851 | −4.7042 | −2.7463 | 1.4479 | 0.0423 |
| | 313.15 | 12.7382 | 2.8314 | −6.5565 | −4.0498 | 5.7818 | 0.0415 |
| | 318.15 | 13.5548 | 2.7117 | −4.3669 | −3.6259 | 4.8646 | 0.0429 |
| $H^E$/J mol$^{-1}$ | 303.15 | 11.6617 | −5.2130 | 4.5427 | 1.6736 | −31.9667 | 0.1688 |
| | 308.15 | 6.3904 | −4.9920 | 0.9841 | 2.7406 | −10.3287 | 0.0507 |
| | 313.15 | 3.1258 | −2.4497 | 4.5043 | 1.1376 | −12.3512 | 0.0630 |
| | 318.15 | 1.8781 | −0.7331 | −1.3985 | −1.9886 | −2.8077 | 0.0467 |
| $\Delta G^{*E}$/J mol$^{-1}$ | 303.15 | 4187.5401 | −2099.0763 | 1612.3419 | 530.2655 | −3151.1456 | 18.8314 |
| | 308.15 | 3468.1010 | −1639.1101 | 874.3378 | 217.0632 | −1107.1057 | 5.8032 |
| | 313.15 | 2605.3642 | −1046.1971 | 896.7585 | 173.6756 | −1378.7058 | 7.8375 |
| | 318.15 | 1349.9850 | −365.0933 | −47.8312 | −136.4053 | −300.7327 | 5.5954 |
| Dimethyl carbonate(1) + *m*−cresol(2) | | | | | | | |
| $V_m^E/10^{-6}$ m$^3$ mol$^{-1}$ | 303.15 | −1.0905 | −0.4010 | 0.2458 | 0.4058 | 0.0859 | 0.0061 |
| | 308.15 | −1.1725 | −0.2975 | 0.2863 | 0.1553 | 0.0091 | 0.0029 |
| | 313.15 | −1.3040 | −0.2378 | 0.1385 | 0.1493 | −0.1227 | 0.0030 |
| | 318.15 | −1.4258 | −0.2476 | −0.1235 | 0.2863 | 0.0988 | 0.0031 |
| $\Delta\beta_{ad}/10^{-12}$ m$^2$ N$^{-1}$ | 303.15 | −1.0223 | −0.0668 | 0.0706 | 0.0836 | −0.0715 | 0.0015 |
| | 308.15 | −1.0733 | −0.0637 | −0.0106 | 0.0850 | 0.0042 | 0.0010 |
| | 313.15 | −1.1360 | −0.0967 | −0.0327 | 0.1106 | 0.0492 | 0.0018 |
| | 318.15 | −1.1990 | −0.0916 | 0.0101 | 0.1040 | 0.0259 | 0.0012 |
| $L_f^E/10^{-11}$ m | 303.15 | −0.0273 | −0.0131 | 0.0190 | 0.0196 | −0.0204 | 0.0004 |
| | 308.15 | −0.0343 | −0.0076 | 0.0013 | 0.0105 | −0.0061 | 0.0002 |
| | 313.15 | −0.0443 | −0.0129 | −0.0108 | 0.0166 | 0.0011 | 0.0002 |
| | 318.15 | −0.0552 | −0.0118 | −0.0098 | 0.0204 | 0.0033 | 0.0001 |
| $\Delta\eta$/mPa s | 303.15 | 2.017 | 0.513 | 0.267 | −0.145 | 0.934 | 0.015 |
| | 308.15 | 1.669 | 0.706 | 0.216 | −0.680 | −0.110 | 0.011 |
| | 313.15 | 1.523 | 0.478 | −0.746 | −0.116 | 0.304 | 0.015 |
| | 318.15 | 1.174 | 0.321 | −0.247 | 0.038 | −1.001 | 0.007 |
| $Z^E/10^{-3}$ kg m$^2$ s$^{-1}$ | 303.15 | 19.8523 | 6.2114 | −2.1500 | −5.4469 | −5.3714 | 0.0830 |

**Table 7** continued

| Property | Temp/K | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| | 308.15 | 20.3540 | 4.8523 | −5.8855 | −1.4946 | −1.2636 | 0.0478 |
| | 313.15 | 21.2748 | 2.7610 | −4.6990 | −0.3236 | 2.6789 | 0.0528 |
| | 318.15 | 21.6590 | 3.2097 | 0.8213 | −2.3862 | −1.5774 | 0.0678 |
| $H^E$/J mol$^{-1}$ | 303.15 | 81.2441 | −33.3108 | 16.3430 | −36.0932 | 47.4777 | 0.2306 |
| | 308.15 | 73.2128 | −26.9523 | 14.8632 | −31.4421 | 27.7995 | 0.1839 |
| | 313.15 | 67.2510 | −25.6425 | 4.8335 | −14.9513 | 18.1092 | 0.1918 |
| | 318.15 | 57.9129 | −23.1007 | 11.9146 | −3.1600 | −13.2263 | 0.1056 |
| $\Delta G^{*E}$/J mol$^{-1}$ | 303.15 | 8799.9934 | −5172.4606 | 2268.9713 | −7700.0330 | 9741.2780 | 39.1586 |
| | 308.15 | 8333.5435 | −4730.8967 | 2315.8892 | −6459.6193 | 7279.2030 | 30.6538 |
| | 313.15 | 7961.1519 | −4608.6836 | 1978.7026 | −4317.8483 | 4896.6149 | 24.4682 |
| | 318.15 | 7207.3766 | −4280.4884 | 2717.6933 | −2217.2257 | 716.7978 | 11.4167 |
| Dimethyl carbonate(1) + *p*−cresol(2) | | | | | | | |
| $V_m^E/10^{-6}$ m$^3$ mol$^{-1}$ | 303.15 | −0.6580 | −0.1000 | 0.6030 | −0.0937 | −0.5316 | 0.0016 |
| | 308.15 | −0.7820 | −0.1943 | 0.2582 | 0.1972 | 0.0073 | 0.0028 |
| | 313.15 | −0.9007 | −0.1750 | 0.0364 | 0.3113 | 0.0219 | 0.0017 |
| | 318.15 | −1.0169 | −0.0972 | −0.1587 | −0.0093 | 0.1084 | 0.0033 |
| $\Delta\beta_{ad}/10^{-12}$ m$^2$ N$^{-1}$ | 303.15 | −0.9984 | 0.0008 | 0.0832 | −0.0442 | −0.0714 | 0.0003 |
| | 308.15 | −1.0722 | −0.0290 | 0.0107 | 0.0296 | 0.0070 | 0.0006 |
| | 313.15 | −1.1381 | −0.0374 | −0.0349 | 0.0571 | 0.0035 | 0.0003 |
| | 318.15 | −1.2122 | −0.0457 | −0.0754 | 0.0373 | 0.0212 | 0.0006 |
| $L_f^E/10^{-11}$ m | 303.15 | −0.0160 | 0.0018 | 0.0208 | −0.0113 | −0.0173 | 0.0001 |
| | 308.15 | −0.0228 | −0.0043 | 0.0039 | 0.0069 | −0.0003 | 0.0002 |
| | 313.15 | −0.0287 | −0.0057 | −0.0076 | 0.0154 | −0.0015 | 0.0001 |
| | 318.15 | −0.0357 | −0.0067 | −0.0184 | 0.0114 | 0.0047 | 0.0002 |
| $\Delta\eta$/mPa s | 303.15 | 0.910 | 0.241 | 0.146 | 0.050 | −0.575 | 0.006 |
| | 308.15 | 0.723 | 0.405 | −0.799 | −0.232 | 0.404 | 0.006 |
| | 313.15 | 0.573 | 0.305 | −0.973 | −0.012 | 0.018 | 0.007 |
| | 318.15 | 0.422 | 0.508 | −0.824 | −0.364 | 0.042 | 0.006 |
| $Z^E/10^{-3}$ kg m$^2$ s$^{-1}$ | 303.15 | −0.0976 | 0.0762 | 0.1077 | 0.0327 | 0.0030 | 0.0662 |
| | 308.15 | 7.4908 | 21.6380 | 13.0178 | 2.9011 | 0.2196 | 1.6802 |
| | 313.15 | 9.8402 | 26.6607 | 15.7732 | 3.4817 | 0.2619 | 1.9198 |
| | 318.15 | 10.8756 | 31.4557 | 18.9487 | 4.2164 | 0.3184 | 2.3604 |
| $H^E$/J mol$^{-1}$ | 303.15 | 74.4800 | −34.3804 | 19.4105 | −23.2412 | 17.8619 | 0.0760 |
| | 308.15 | 67.9689 | −28.4917 | 5.6480 | −19.7854 | 24.6408 | 0.0809 |
| | 313.15 | 60.6792 | −25.8148 | 3.2617 | −7.8761 | 8.0971 | 0.0899 |
| | 318.15 | 51.8497 | −17.4674 | −1.1871 | −8.9811 | 7.5789 | 0.0670 |
| $\Delta G^{*E}$/J mol$^{-1}$ | 303.15 | 8504.6790 | −5296.9011 | 2889.1236 | −6075.9735 | 6516.3861 | 22.2421 |
| | 308.15 | 8136.7024 | −4864.2268 | 2033.1557 | −5153.8986 | 6057.6214 | 16.9438 |
| | 313.15 | 7661.8829 | −4637.3061 | 2090.4911 | −3317.0892 | 3358.3228 | 10.4096 |
| | 318.15 | 6907.7074 | −3781.9127 | 1443.0684 | −2600.3942 | 2550.6892 | 5.9372 |

Fig. 4 shows excess partial molar volumes are negative for the three studied cresol systems. It supports the existence of hetero-molecular association among the component molecules of binary mixture. Negative excess partial molar volumes indicate that interaction is stronger between unlike molecules than like molecules [38].

The existence of strong interactions between dimethyl carbonate and isomeric cresols can be well supported by

**Table 8** Values of variation of excess enthalpy with pressure against mole fraction, $x_1$ of DMC for binary mixtures

| DMC + OC | | DMC + MC | | DMC + PC | |
|---|---|---|---|---|---|
| $x_1$ | $\left(\frac{\partial H_m^E}{\partial P}\right)_{303.15K}$ /($10^{-6}$ $m^3$ $mol^{-1}$) | $x_1$ | $\left(\frac{\partial H_m^E}{\partial P}\right)_{303.15K}$ /($10^{-6}$ $m^3$ $mol^{-1}$) | $x_1$ | $\left(\frac{\partial H_m^E}{\partial P}\right)_{303.15K}$ /($10^{-6}$ $m^3$ $mol^{-1}$) |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1197 | −0.0391 | 0.1208 | −0.1113 | 0.1207 | −0.0641 |
| 0.2343 | −0.0621 | 0.2362 | −0.1994 | 0.2360 | −0.1112 |
| 0.3441 | −0.0841 | 0.3464 | −0.2667 | 0.3463 | −0.1447 |
| 0.4494 | −0.1018 | 0.4519 | −0.2768 | 0.4517 | −0.1637 |
| 0.5504 | −0.0946 | 0.5529 | −0.2585 | 0.5527 | −0.1584 |
| 0.6474 | −0.0779 | 0.6498 | −0.2211 | 0.6496 | −0.1316 |
| 0.7407 | −0.0451 | 0.7427 | −0.1681 | 0.7425 | −0.0931 |
| 0.8304 | −0.0197 | 0.8319 | −0.1052 | 0.8317 | −0.0582 |
| 0.9168 | −0.0069 | 0.9176 | −0.0589 | 0.9175 | −0.0271 |
| 1.0000 | 0.0000 | 1.0000 | 0.0000 | 1.0000 | 0.0000 |

(DMC (1) + OC/MC/PC (2)) at $T = 303.15$ K

other derived excess/deviation parameters such as deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess free length ($L_f^E$), excess acoustic impedance ($Z^E$), deviation in viscosity ($\Delta\eta$), excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$),excess enthalpy ($H^E$), and certain molecular properties are also calculated from Sehgal's equations in conjunction with nonlinear parameters; excess values of nonlinear parameters are evaluated using semi-empirical relations.

Like excess molar volume, adiabatic compressibility is related to internal organisation of molecules. Adiabatic compressibility, $\beta_{ad}$, of a mixture is determined by using Eq. (8). The deviations in adiabatic compressibility are graphically represented in Fig. 5a–c as a function of mole fraction of DMC at $T =$ (303.15, 308.15, 313.15 and 318.15) K. $\Delta\beta_{ad}$ values are negative for all binary mixtures of DMC + isomeric cresols over the entire range of composition at all temperatures. According to Fort and Moore [39], a negative excess compressibility is an indication of strong hetero-molecular interaction in the liquid mixtures which is attributable to charge transfer, dipole–dipole, dipole-induced dipole interactions and hydrogen bonding between unlike components, while a positive sign indicates weak interaction and is attributed to dispersion forces (London forces). Negative sign in adiabatic compressibility of mixture indicates that the mixture is less compressible than that of pure liquids which means molecules in the mixture are more effectively bind than in their pure form. In general, sign and magnitude of $\Delta\beta_{ad}$ depends on following factors:

(a) Difference in molecular size and shape of the molecules
(b) Destruction of H-bonding
(c) H-bonding association
(d) Complex formation between component molecules.

First two factors lead to positive contribution to $\Delta\beta_{ad}$, and next two factors leads to negative contribution. Figure 5a–c shows that the variation is nonlinear and at any particular concentration negative values of adiabatic compressibility increases with increase in temperature. The negative deviation in adiabatic compressibility reaches a peak value at about 0.4519 (in *m*-cresol binary system) mole fraction of dimethyl carbonate. The negative $\Delta\beta_{ad}$ values indicate closer approach of unlike molecules and hence stronger interaction between components of mixtures at all temperatures. This supports the inference drawn from $V_m^E$.

The intermolecular free length is the distance between the surfaces of neighbouring molecules. The sign and magnitude of the computed values of $L_f^E$ was found to depend on several contributions which are physical or/and chemical in nature. The physical contributions comprise dispersion forces or weak Van der Walls forces, whereas chemical contributions involve breaking up of hydrogen-bonded structures which lead to positive $L_f^E$ values. Specific interactions such as complex formation, dipole–dipole interactions between component molecules and formation of new hydrogen bonds lead to negative $L_f^E$ values, making the system more ordered due to increased intermolecular interactions [40]. Both adiabatic compressibility and free length are the deciding factors of the transmission of ultrasonic velocity in liquid systems. The variation of $L_f^E$ with mole fraction of DMC at 308.15 K for all the binary mixtures under study is illustrated in Fig. 6. Negative $L_f^E$ values are observed for the binary mixtures of (DMC + *m*-cresol) and (DMC + *p*-cresol) at all the temperatures and over the entire range of mole fraction, indicating existence of strong specific interaction. In case of DMC and *o*-cresol binary system, at 303.15 K, $L_f^E$ values are positive. It may be due to the occurrence of steric crowd around –OH of *o*-cresol. As the temperature increases from (308.15 to 318.15) K, $L_f^E$ becomes more negative. In hetero-molecular interaction between the component molecules of the mixtures, negative values of excess intermolecular free length $L_f^E$ indicate that sound waves cover longer distances due to decrease in intermolecular free length reflecting the dominant nature of molecular association among components of hetero molecules [2]. The negative values of $L_f^E$ are generally due to the specific interactions between unlike molecules in the liquid mixture and also due to the structural readjustments

**Table 9** Computed excess values of $(B/A)^E$, cohesive energy ($\Delta A$), Van der Waal's constants ($a$ and $b$), distance of closest approach ($d$), from nonlinear parameters proposed by Hartmann–Balizar ($B$ and $H$) and Ballou relations for DMC + OC, DMC + MC and DMC + PC at 303.15 K

| $(B/A)^E$ | $\Delta A$/J mol$^{-1}$ | $a$/N m$^4$ mol$^{-1}$ | $b/10^{-3}$ m$^3$ mol$^{-1}$ | $d/10^{-10}$ m | $(B/A)^E$ | $\Delta A$/J mol$^{-1}$ | $A$/N m$^4$ mol$^{-1}$ | $B/10^{-3}$ m$^3$ mol$^{-1}$ | $D/10^{-10}$ m |
|---|---|---|---|---|---|---|---|---|---|
| DMC + OC | Hartmann–Balizar | | | | Ballou | | | | |
| 0.0000 | −424,167.8387 | 2.5940 | 0.0938 | 4.2055 | 0.0000 | −474,539.7771 | 2.9021 | 0.0949 | 4.2222 |
| −0.0406 | −388,682.6641 | 2.3237 | 0.0907 | 4.1596 | −0.0498 | −432,104.4953 | 2.5833 | 0.0919 | 4.1769 |
| −0.0710 | −356,689.3107 | 2.0859 | *0.0878* | *4.1138* | *−0.0870* | *−394,121.9404* | *2.3048* | 0.0889 | 4.1316 |
| −0.0917 | −327,786.7947 | 1.8759 | 0.0849 | 4.0680 | −0.1122 | −360,049.3762 | 2.0605 | 0.0860 | 4.0862 |
| −0.1035 | −301,679.2705 | 1.6904 | 0.0820 | 4.0219 | −0.1267 | −329,482.0565 | 1.8462 | 0.0832 | 4.0406 |
| −0.1058 | −277,925.2702 | 1.5258 | 0.0792 | 3.9757 | −0.1295 | −301,852.4514 | 1.6572 | 0.0804 | 3.9948 |
| −0.0998 | −256,370.2594 | 1.3797 | 0.0765 | 3.9291 | −0.1222 | −276,942.0924 | 1.4904 | 0.0776 | 3.9486 |
| −0.0858 | −236,761.1636 | 1.2498 | 0.0738 | 3.8821 | −0.1050 | −254,422.0721 | 1.3430 | 0.0749 | 3.9020 |
| −0.0644 | −218,927.8154 | 1.1339 | 0.0711 | 3.8343 | −0.0789 | −234,065.9932 | 1.2123 | 0.0722 | 3.8544 |
| −0.0359 | −202,666.6496 | 1.0301 | 0.0684 | 3.7853 | −0.0439 | −215,613.7691 | 1.0959 | 0.0695 | 3.8056 |
| 0.0000 | −187,796.4081 | 0.9370 | 0.0657 | 3.7351 | 0.0000 | −198,836.2351 | 0.9921 | 0.0668 | 3.7556 |
| DMC + MC | Hartmann–Balizar | | | | Ballou | | | | |
| 0.0000 | −407,840.0734 | 2.5212 | 0.0943 | 4.2136 | 0.0000 | −454,615.6097 | 2.8104 | 0.0955 | 4.2305 |
| −0.0371 | −374,915.9199 | 2.2611 | 0.0911 | 4.1648 | −0.0454 | −415,437.6879 | 2.5055 | 0.0922 | 4.1823 |
| −0.0648 | −345,247.4634 | 2.0328 | 0.0879 | 4.1165 | −0.0793 | −380,374.7017 | 2.2396 | 0.0891 | 4.1345 |
| −0.0832 | −318,389.3650 | 1.8315 | 0.0849 | 4.0685 | −0.1018 | −348,841.0311 | 2.0066 | 0.0861 | 4.0869 |
| −0.0932 | −294,068.9116 | 1.6544 | 0.0820 | 4.0212 | −0.1141 | −320,469.6371 | 1.8029 | 0.0831 | 4.0400 |
| −0.0947 | −271,939.4255 | 1.4975 | 0.0791 | 3.9741 | −0.1159 | −294,812.6543 | 1.6234 | 0.0803 | 3.9933 |
| −0.0890 | −251,858.0800 | 1.3584 | 0.0764 | 3.9271 | −0.1089 | −271,670.7921 | 1.4652 | 0.0775 | 3.9466 |
| −0.0764 | −233,586.9618 | 1.2347 | 0.0736 | 3.8799 | −0.0935 | −250,737.7146 | 1.3254 | 0.0748 | 3.8997 |
| −0.0570 | −216,916.7551 | 1.1244 | 0.0710 | 3.8323 | −0.0697 | −231,746.2666 | 1.2013 | 0.0721 | 3.8525 |
| −0.0308 | −201,665.5735 | 1.0253 | 0.0683 | 3.7839 | −0.0377 | −214,465.7864 | 1.0904 | 0.0694 | 3.8042 |
| 0.0000 | −187,796.4081 | 0.9370 | 0.0657 | 3.7351 | 0.0000 | −198,836.2351 | 0.9921 | 0.0668 | 3.7556 |
| DMC + PC | Hartmann–Balizar | | | | Ballou | | | | |
| 0.0000 | −411,110.7992 | 2.5395 | 0.0943 | 4.2138 | 0.0000 | −458,602.9154 | 2.8328 | 0.0955 | 4.2307 |
| −0.0373 | −377,546.3770 | 2.2765 | 0.0911 | 4.1658 | −0.0456 | −418,621.1379 | 2.5242 | 0.0923 | 4.1832 |
| −0.0650 | −347,322.5128 | 2.0457 | 0.0881 | 4.1181 | −0.0796 | −382,868.5139 | 2.2550 | 0.0892 | 4.1360 |
| −0.0836 | −320,028.0936 | 1.8424 | 0.0850 | 4.0706 | −0.1024 | −350,797.3570 | 2.0195 | 0.0862 | 4.0890 |
| −0.0936 | −295,321.1412 | 1.6628 | 0.0821 | 4.0232 | −0.1146 | −321,954.4762 | 1.8128 | 0.0833 | 4.0421 |
| −0.0953 | −272,899.5158 | 1.5039 | 0.0792 | 3.9760 | −0.1167 | −295,943.6161 | 1.6309 | 0.0804 | 3.9952 |
| −0.0896 | −252,553.2526 | 1.3632 | 0.0765 | 3.9287 | −0.1097 | −272,484.5686 | 1.4707 | 0.0776 | 3.9483 |
| −0.0767 | −234,042.8093 | 1.2380 | 0.0737 | 3.8813 | −0.0939 | −251,268.1272 | 1.3291 | 0.0749 | 3.9012 |
| −0.0574 | −217,206.1008 | 1.1264 | 0.0710 | 3.8333 | −0.0703 | −232,080.8719 | 1.2035 | 0.0721 | 3.8534 |
| −0.0318 | −201,847.9969 | 1.0266 | 0.0683 | 3.7846 | −0.0390 | −214,675.6048 | 1.0918 | 0.0695 | 3.8049 |
| 0.0000 | −187,796.4081 | 0.9370 | 0.0657 | 3.7351 | 0.0000 | −198,836.2351 | 0.9921 | 0.0668 | 3.7556 |

in the liquid mixture towards a less compressible phase and closer packing of the molecules [41].

The acoustic impedance at a particular frequency indicates how much sound pressure is generated by a given air vibration at that frequency. Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems [42]. The variation of $Z^E$ with the mole fraction of DMC at 308.15 K is shown in Fig. 7. From the figure, it is shown that $Z^E$ is positive for all the systems and at all temperatures. The positive values of $Z^E$ are attributed to

**Table 10** FTIR stretching frequencies of pure components and their equimolar (1:1) binary mixtures of DMC with isomeric cresols at 298.15 K

| Compound | Band | $\upsilon/\mathrm{cm}^{-1}$ | $\Delta\upsilon/\mathrm{cm}^{-1}$ |
|---|---|---|---|
| Dimethyl carbonate | C=O Str. | 1756 | – |
| *m*-cresol | O–H Str. | 3328 | – |
| *p*-cresol | O–H Str. | 3319 | – |
| *o*-cresol | O–H Str. | 3421 | – |
| DMC + MC | O–H Str. | 3295 | 33–(OH) |
| DMC + PC | O–H Str. | 3305 | 14–(OH) |
| DMC + OC | O–H Str. | 3415 | 6–(OH) |

the presence of specific interactions between hetero molecules [43]. With increase in temperature, absolute values of $Z^{\mathrm{E}}$ increase linearly, which further supports increase in intermolecular interactions among binary liquids with temperature.

Viscosity ($\eta$) is a measure of cohesiveness or rigidity present between the molecules in a liquid. The variation of deviation in viscosity, $\Delta\eta$, with the mole fraction of DMC for all the binary mixtures at 308.15 K is shown in Fig. 8. Similar trend was observed at other temperatures also. The deviations in $\Delta\eta$ values are found to be positive, opposite to the sign of excess molar volumes for MC, PC binary mixtures, which is in agreement with the views proposed by Brocos et al. [44, 45]. A correlation between the sign of $\Delta\eta$ and sign of $V_{\mathrm{m}}^{\mathrm{E}}$ has been observed for a number of binary solvent systems [32, 46], i.e. $\Delta\eta$ is positive when $V_{\mathrm{m}}^{\mathrm{E}}$ is negative and vice versa. Our results support this correlation. Specific type of interactions such as dipole–dipole interactions, hydrogen bond formation and accommodation of small size molecules into the voids of larger molecules makes the structure more compact and results in positive $\Delta\eta$ values [47]. In case of *meta*- and *para*-cresols, positive $\Delta\eta$ values refer to the formation of intermolecular hydrogen bonds, dipole–dipole interactions. In case of *o*-cresol viscosity, deviation is negative, showing dominance of steric effect, which opposes close proximity of constituent molecules, over the intermolecular hydrogen bond formation among the binary mixtures. Rosal et al. [22] reported negative viscosity deviation in *o*-cresol mixture and positive deviation in *meta*- and *para*-cresol mixture. He suggested that along with intermolecular H-bond formation, other factors such as average degree of association, shape and size of the molecules affect the viscosity deviation. The sign and magnitude of viscosity deviation refers to the strength of interaction between unlike molecule. The π-electron density in derivatives of benzene ring depends upon the group that is attached to it. There may be some n…….π interactions between the pair of electrons on carbonyl oxygen of ester and π electron clouds of benzene ring in cresol. This was further supported by Yang et al. [48].

Available energy of a system to do work at constant temperature and pressure is called Gibbs free energy. In order to elucidate the forces that are acting between unlike molecules, excess Gibbs free energy of activation for viscous flow is essential. The values of excess energy of activation of viscous flow for the various mole fractions of DMC $(x_1)$ at four different temperatures for all the binary mixtures are listed in Table 6. The values of $\Delta G^{*\mathrm{E}}$ for the studied binaries at 308.15 K are graphically represented in Fig. 9 as a function of mole fraction of DMC at T = 308.15 K. Perusal of Fig. 9 shows excess Gibbs free energy of activation of viscous flow is positive over the entire composition range for all the three binaries. The more positive values of $\Delta G^{*\mathrm{E}}$ for DMC + MC system indicate that the interactions are predominant compared to DMC + PC and DMC + OC systems. Similar trend was observed at other temperatures also. It is a well-known fact that negative values of $\Delta G^{*\mathrm{E}}$ indicate the presence of weak physical forces such as dispersive forces in the system [49]. On the other hand, positive values of it suggest strong specific interactions between molecules in study [50]. This also supports the conclusions drawn from our earlier findings.

Enthalpy $H$ is a thermodynamic quantity, equivalent to the total heat content of a system. Table 6 illustrates that the values of $H^{\mathrm{E}}$ are found to be positive over the entire mole fraction range at all temperatures investigated for the studied binary mixtures. The variation of $H^{\mathrm{E}}$ with mole fraction of DMC at 308.15 K for all the binary mixtures under study is illustrated in Fig. 10. The sign and magnitude of $H^{\mathrm{E}}$ values of liquid mixtures reflects the interactions between like and unlike molecules. In the standard mixing process, interactions between like species are disrupted, and interactions between unlike species (DMC and cresols) are promoted. Hence, in this case, unlike attractions are stronger giving $H^{\mathrm{E}}$ is positive, i.e. the mixing process is endothermic [51].

All the above-explained excess/deviation quantities are correlated by using Redlich–kister polynomial Eq. (14) as a function of temperature. The fitting coefficients $A_{i-1}$ are listed in Table 7 along with their standard deviation $\sigma$ (root-mean-square deviation) by using Eq. (15).

Table 8 shows that variation of excess molar enthalpy with pressure $\left(\frac{\partial H_{\mathrm{m}}^{\mathrm{E}}}{\partial P}\right)$ for all the binary mixtures under study at 303.15 K has negative values in the whole composition range. This reflects increase in attraction forces between two components of binary mixture with increase in pressure. Therefore, contraction in the volume of the mixture is possible by increasing pressure [52].

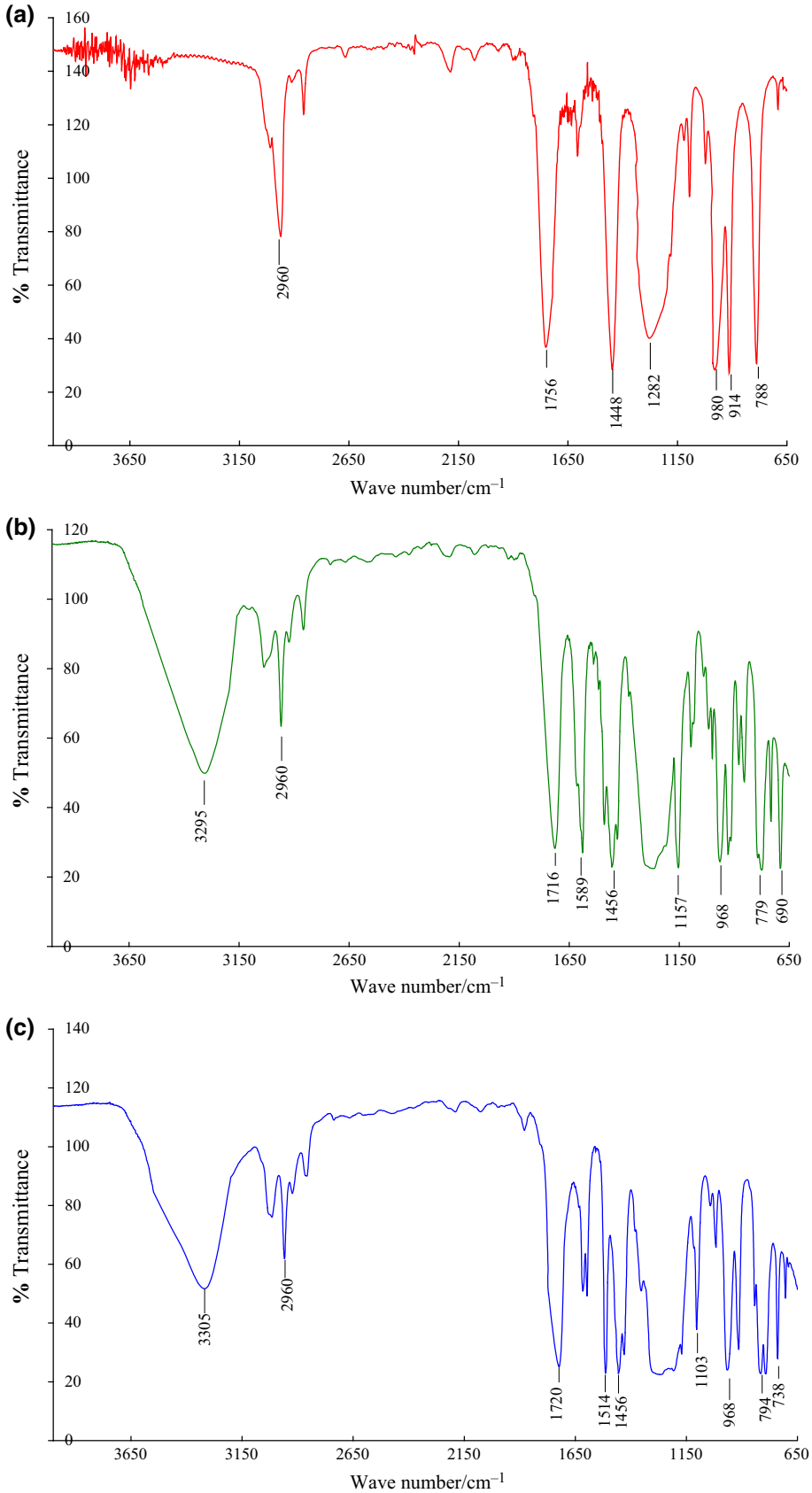
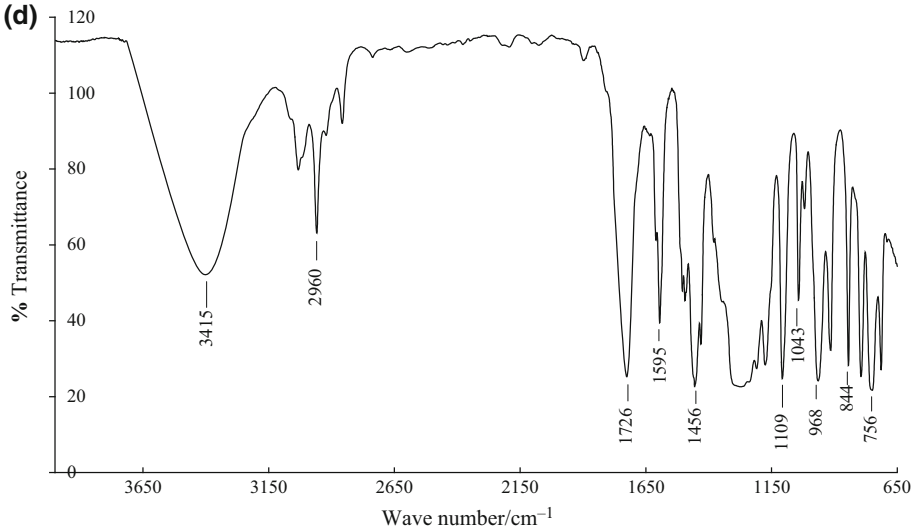



**Fig. 11** **a** FTIR spectrum of dimethyl carbonate (*red colour*), **b** FTIR spectrum of 1:1 mixture of DMC + MC (*green colour*), **c** FTIR spectrum of 1:1 mixture of DMC + PC (*blue colour*), **d** FTIR spectrum of 1:1 mixture of DMC + OC (*black colour*) at 298.15 K. (Color figure online)

**Fig. 11** continued




The nonlinearity parameter ($B/A$) is a measure of the nonlinearity of the equation of state for a fluid. It plays a significant role in acoustics, from underwater acoustics to biology and medicine. The nonlinearity parameter determines distortion of a finite amplitude wave propagating in the fluid. Further, it can be related to the molecular dynamics of the medium and it can provide information about structural properties of medium, internal pressures, clustering and intermolecular spacing, etc. Importance of the $B/A$ parameter increases with the development of high-pressure technologies of food processing and preservation.

An attempt has been made to evaluate the values of molecular properties of the liquid mixtures using nonlinearity parameter ($B/A$) values from semi-empirical relations proposed by Hartmann–Balizar (H and B) [53] and Ballou [54] with the use of Sehgal's relations [55]. The computed values of cohesive energy ($\Delta A$), Van der Waal's constants ($a$ and $b$) and distance of closest approach ($d$) are given in Table 9. Excess values of ($B/A$) are found to be negative for all the three binaries at 303.15 K. Negative values of $(B/A)^{E}$ indicate strong interaction, and a positive value of $(B/A)^{E}$ indicates a relatively weak interaction between unlike molecules [56]. Thus, negative values of $(B/A)^{E}$ also support the existence of strong interactions in the present binary systems under study.

## FTIR studies

FTIR spectroscopy has been extensively used to study molecular interaction in terms of hydrogen bonding in binary liquid mixtures. The present study takes the support of FTIR to explain the intermolecular association in terms of hydrogen bonding. The values of the –OH stretching and –CO stretching frequencies of pure and equimolar binary liquids are given in Table 10 at 298.15 K. In general, intermolecular hydrogen bonds gives rise to broad bands, whereas bands arising from intramolecular hydrogen bonds are sharp and well defined [57]. Pure liquids show only broad bands in the (3600–3200) $cm^{-1}$ (hydrogen-bonded –OH stretching frequency) [28]. Pure components namely *o*-cresol, *m*-cresol and *p*-cresol show characteristic (–OH stretching) absorption peaks at 3421, 3328, 3319 $cm^{-1}$, respectively. Figure 11 shows the resultant absorption bands of DMC and 1:1 binary liquids having hydrogen-bonded stretching frequencies, i.e. DMC with OC, MC and PC.

From the recorded FTIR spectra (Fig. 11a), it is evident that in dimethyl carbonate, C=O stretching band appears at 1756 $cm^{-1}$ [58], C–H stretch at of methyl group at 2960 $cm^{-1}$, C–O stretching at 1282 $cm^{-1}$ and C–H deformation band at 1448 $cm^{-1}$. Perusal of Fig. 11b–d, for 1:1 binary mixtures of DMC and isomeric cresols, shift of O–H bond stretching frequency is as follows: in binary system of *m*-cresol $\Delta\nu$ shows shift, i.e. from 3328 to 3295 $cm^{-1}$; in binary system of *p*-cresol, shift of $\Delta\nu$ is from 3319 $cm^{-1}$ to 3305 $cm^{-1}$ and in *o*-cresol binary mixture, shift is from 3421 $cm^{-1}$ to 3415 $cm^{-1}$. It is a well-known fact that if $\Delta\nu$ shows positive shift (shift towards higher frequency), there is weakened intermolecular association and if $\Delta\nu$ shows shift towards lower frequency indicates strong association between unlike molecules [57, 59]. Negative shifts (shifts towards lower frequency) are observed for all the binary mixtures of DMC and isomeric cresols, indicating existence of intermolecular hydrogen bonding between oxygen atom of –CO group of DMC and hydrogen atom of –OH group of isomeric cresols, which further supports the existence of strong interactions in the binary mixtures of DMC and isomeric cresols. The electrostatic force of attraction with which hydrogen atom of one molecule (cresol) is attracted

by the oxygen atom of another molecule (DMC) makes it easier to pull hydrogen away from oxygen atom (O···H–O). Thus, small energy will be required to stretch such a bond (O–H); hence, absorption occurs at lower frequency. Based on the magnitude of shift in the stretching frequencies of O–H band in the studied binaries, the order of strong interactions is as follows: (DMC + *m*-cresol > (DMC + *p*-cresol) > (DMC + *o*-cresol). Thus, FTIR also supports the inferences drawn from excess/deviation properties.

## Conclusions

(a) Ultrasonic velocities ($u$), densities ($\rho$) and viscosities ($\eta$) for binary liquids of DMC with cresols are determined experimentally at $T =$ (303.15, 308.15, 313.15 and 318.15) K over the entire composition range.

(b) The $V_m^E$, $\Delta\beta_{ad}$, $L_f^E$, $Z^E$, $\Delta\eta$, $\Delta G^{*E}$ and $H^E$ are calculated using experimental data at four different temperatures. The excess/deviation properties are fitted to Redlich–Kister-type polynomial equation to derive their coefficients and standard deviations. The observed negative values of $V_m^E$, $\Delta\beta_{ad}$,$L_f^E$ and positive values of $Z^E$, $\Delta\eta$, $\Delta G^{*E}$ $H^E$ clearly indicate dominance of specific interaction among the binary liquids. The order of strong interaction among the component molecules in binary liquids is as follows: (DMC + MC) > (DMC + PC) > (DMC + OC). The increase in strength of interaction with temperature is as follows: (303.15 < 308.15 < 313.15 < 318.15) K.

(c) Further, the values of $\bar{V}_{m,1}, \bar{V}_{m,2}$ and $\bar{V}^E_{m,1}, \bar{V}^E_{m,2}$ are calculated from experimental data. The observed lower values of partial molar volumes in binary mixture when compared with the respective pure components and negative values of excess partial molar volumes indicate strong interaction and support the $V_m^E$. Furthermore, variation of excess molar enthalpy with pressure at $T = 303.15$ K is also studied for all the systems.

(d) Nonlinear parameter ($B/A$) is evaluated using semi-empirical relations, and certain molecular properties are calculated from Sehgal's equations. Negative values of $(B/A)^E$ for all the three binaries at 303.15 K also agree with the experimental results and significantly indicate the existence of significant molecular interaction.

(e) Negative shift of $\Delta\nu$ in the –OH bond stretching frequencies of isomeric cresols in the binary mixtures with respect to the pure cresols indicates hetero-molecular hydrogen bond formation which further supports the experimental results.

**Acknowledgements** One of the authors, Sk.B. wishes to thank Department of chemistry, Acharya Nagarjuna University for providing laboratory facilities. She gratefully acknowledges the technical support for the IR studies received from Department of Physics, Acharya Nagarjuna University.

## References

1. Oswal SL, Desai HS. Studies of viscosity and excess molar volume of binary mixtures: 4. 1-Alkanol + tri-*n*-butylamine mixtures at 303.15 and 313.15 K. Fluid Phase Equilib. 2003;204:281–94.
2. Oswal SL, Patel IN. Excess molar volumes of binary mixtures of alkyl acetates with hexane, tetrachloromethane, and trichloromethane. Fluid Phase Equilib. 1998;149:249–59.
3. Kinart CM, Kinart WJ, Cwiklinska A. 2-Methoxyethanol-tetrahydrofuran binary liquid system viscosities, densities, excess molar volumes and excess gibbs activation energies of viscous flow at various temperatures. J Therm Anal Calorim. 2002;68:307–17.
4. Pistoia G, editor. Lithium batteries: new materials, developments and perspectives, industrial chemistry library, vol. 5. Amsterdam: Elsevier; 1994.
5. Tobishima SI, Arakawa M, Yamaki JI. Electrolytic properties of $LiClO_4$—propylene carbonate mixed with amide-solvents for lithium batteries. Electrochim Acta. 1988;33:239–44.
6. Romano E, Trenzado JL, González E, Matos JS, Segade L, Jiménez E. Thermophysical properties of four binary dimethyl carbonate+ 1-Alcohol Systems at 288.15–313.15 K. Fluid Phase Equilib. 2003;211:219–40.
7. Kavitha Ch, Ratnakar A, Durga Bhavani M, Narendra K. Study of Molecular Interactions in Ternary Mixtures of Quinoline with o-cresol, m-cresol and p-cresol in Methanol at T = 303.15, 308.15, 313.15, and 318.15 K. Int Res J Pure Appl Chem. 2014;4:213–26.
8. Ranganayakulu SV, Sreenivasa Reddy C, Venkateswar S, Linga RD. Ultrasonic studies of the binary mixtures of ethyl acetate and cresols—applications of Kosower and Dimroth treatments. Mater Chem Phys. 2005;90:213–20.
9. Ahluwalia R, Gupta R, Vashisht JL, Wanchoo RK. Physical properties of binary liquid systems: ethanoic acid/propanoic acid/butanoic acid with cresols. J Solut Chem. 2013;42:945–66.
10. Fakruddin SK, Srinivasu CH, Narendra K. Acoustical parameters of some binary liquid mixtures containing heterocyclic aromatic compound with methylphenols at different temperatures. Int J Res Chem Environ. 2012;2:164–7.
11. Bhatia SC, Rani R, Bhatia R, Anand H. Volumetric and ultrasonic behaviour of binary mixtures of 1-nonanol with o-cresol, m-cresol, p-cresol and anisole at T = (293.15 and 313.15) K. J Chem Thermodyn. 2011;43:479–86.
12. Lugo L, Comunas MJP, Lopez ER, Fernandez J. (p, Vm, T, *x*) measurements of dimethyl carbonate + octane binary mixtures I. Experimental results, isothermal compressibilities, isobaric expansivities and internal pressures. Fluid Phase Equilib. 2001;186:235–55.
13. Shin SH, Jeong IY, Jeong YS, Park SJ. Solid-liquid equilibria and the physical properties of binary systems of diphenyl carbonate, dimethyl carbonate, methyl phenyl carbonate, anisole, Methanol and Phenol. Fluid Phase Equilib. 2014;376:105–10.
14. Iglesias-Otero MA, Troncoso J, Carballo E, Romani L. Density and refractive index for binary systems of the ionic liquid [Bmim][BF4] with methanol, 1,3-dichloropropane, and dimethyl carbonate. J Solut Chem. 2007;36:1219–30.

15. Chen F, Yang Z, Chen Z, Hu J, Chen C, Cai J. Density, viscosity, speed of sound, excess property and bulk modulus of binary mixtures of gamma-butyrolactone with acetonitrile, dimethyl carbonate, and tetrahydrofuran at temperatures (293.15 to 333.15) K. J Mol Liq. 2015;209:683–92.
16. Vogel AI. Vogel's textbook of practical organic chemistry. 5th ed. New York: Wiley; 1989.
17. Riddick JA, Bunger WB, Sakano TK. Organic solvents: physical properties and methods of purification. 4th ed. New York: Wiley; 1986.
18. Ren R, Zuo Y, Zhou Q, Zhang H, Zhang S. Density, excess molar volume and conductivity of binary mixtures of the ionic liquid 1,2-dimethyl-3- hexylimidazolium bis(trifluoromethylsulfonyl)imide and dimethyl carbonate. J Chem Eng Data. 2011;56:27–30.
19. Sharma S, Patel P, Bhalodia J. Volumetric and viscometric study of binary mixtures of 1,8-cineole with o-, m- and p-cresol at 303.15, 308.15 and 313.15 K. J Phys Chem Liq. 2016;54:42–55.
20. Pereiro AB, Rodríguez 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. 2004;49:1392–9.
21. Pal A, Dass G. Excess molar volumes and viscosities of diethylene glycol diethyl ether with dimethyl carbonate, diethyl carbonate, and propylene carbonate at (298.15, 308.15, and 318.15) K. J Chem Eng Data. 2000;45:487–91.
22. Rosal R, Medina I, Forster E, Maclnnes J. Viscosities and densities for binary mixtures of cresols. Fluid Phase Equilib. 2003;211:143–50.
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. 2006;51:935–9.
24. Umadevi P, Rambabu K, Rao MN, Rao KS, Rambabu C. Densities, adiabatic compressibility, free-length, viscosities and excess volumes of p-cresol(1)+ dimethyl sulfoxide (2), + dimethyl formamide (2), and+ 1,4-dioxane at 30315-31815K. Phys Chem Liq. 1995;30:29–46.
25. Rodríguez A, Canosa J, Tojo J. Physical properties of binary mixtures (dimethyl carbonate + alcohols) at several temperatures. J Chem Eng Data. 2001;46:1476–86.
26. Pardo JM, González-Salgado D, Tovar CA, Cerdeiriña CA, Carballo E, Romaní L. Comparative study of the thermodynamic behaviour of the binary mixtures dimethyl carbonate+ (benzene, *n*-heptane, cyclohexane, or toluene). Can J Chem. 2002;80:370–8.
27. Bhatia SC, Rani R, Bhatia R. Densities, speeds of sound and refractive indices of binary mixtures of decan-1-ol with anisole, o-cresol, m-cresol, and p-cresol at t = (298.15, 303.15, and 308.15) K. J Chem Eng Data. 2011;56:1669–74.
28. Raveendra M, Chandrasekhar M, Narasimharao C, Venkatramanna L, Siva Kumar K, Dayananda Reddy K. Elucidation of hydrogen bonding formation by a computational, FT-IR spectroscopic and theoretical study between benzyl alcohol and isomeric cresols. RSC Adv. 2016;6:27335–48.
29. Santhi N, Sabarathinam PL, Emayavaramban M, Gopi C, Manivannan C. Molecular interaction studies in binary liquid mixtures from ultrasonic data. E-J Chem. 2010;7:648–54.
30. Weissberger A. Techniques of organic chemistry. 3rd ed. New York: Wiley; 1965.
31. Redlich O, Kister AT. Thermodynamic of non electrolyte solutions: algebraic representation of thermodynamic properties and the classification of solutions. Ind Eng Chem. 1948;40:345–8.
32. Rama Rao GV, Sarma AV, Rambabu C. Excess volumes, deviation in viscosities and compressibilities of binary mixtures consisting of morpholine, piperidine with methanol and pyridine at different temperatures. Indian J Pure Appl Phys. 2004;42:820–6.
33. Ali A, Nain AK, Chand D, Lal D. Ultrasonic, volumetric and viscometric studies of molecular interactions in binary mixtures of dimethylsulphoxide with polar substituted cyclohexanes at 30°C. Phys Chem Liq. 2007;45:79–91.
34. Ali A, Nain AK, Sharma VK, Ahmad S. Study of molecular interaction in ternary mixtures through ultrasonic speed measurements. Phys Chem Liq. 2004;42:375–83.
35. Rajagopal K, Chenthilnath S. Excess parameter studies on the binary mixtures of toluene with ketones at different temperatures. J Chem Thermodyn. 2010;42:675–83.
36. Sankar MG, Ponneri V, Kumar KS, Sakamuri S. Molecular interactions between amine and cyclic ketones at different temperatures. J Therm Anal Calorim. 2014;115:1821–7.
37. Srinivasa Reddy M, Nayeem SM, Raju K, Srinivasa Rao V, Hari Babu B. The study of solute–solvent interactions in 1-ethyl-3-methylimidazolium ethylsulfate +2-ethoxyethanol from density, speed of sound and refractive index measurements. J Mol Liq. 2016;218:83–94.
38. Nain AK. Densities and volumetric properties of (acetonitile + an amide) at temperatures between 293.15 and 318.15 K. J Chem Thermodyn. 2006;38:1362–70.
39. Fort RJ, Moore WR. Adiabatic compressibilities of binary liquid mixtures. J Trans Faraday Soc. 1965;61:2102–11.
40. Nayeem Md Sk, Kondaiah M, Sreekanth K, Srinivasa Reddy M, Krishna Rao D. Thermoacoustic, volumetric, and viscometric investigations in the binary mixtures of 1,4-dioxane with n-hexane or n-heptane or n-octane. J Therm Anal Calorim. 2016;123:2241–2255.
41. Govardhana Rao S, Madhu Mohan T, Vijaya Krishna T, Srinivasa Krishna T, Subba RB. Density, refractive index, and speed of sound of the binary mixture of 1-butyl-3-methylimidazolium tetrafluoroborate +*n*-vinyl-2-pyrrolidinone from *t* = (298.15 to 323.15) K at atmospheric pressure. J Chem Eng Data. 2015;60:886–94.
42. Srinivasa Reddy M, Nayeem S, Raju K, Hari BB. The study of solute–solvent interactions in 1-ethyl-3-methylimidazolium tetrafluoroborate+ 2-ethoxyethanol from density, speed of sound, and refractive index measurements. J Therm Anal Calorim. 2016;124:959–71.
43. Nayeem Md Sk, Kondaiah M, Sreekanth K, Rao DK. Comparative study of molecular interactions in aromatic, cyclic and aliphatic ketones with 1-octanol at 308.15 K: an insight from ultrasonic velocity and density. J Mol Liq. 2015;207:286–93.
44. Brocos P, Piñeiro Á, Bravo R, Amigo A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. Phys Chem Chem Phys. 2003;5:550–7.
45. Pineiro Á, Brocos P, Amigo A, Pintos M, Bravo R. Prediction of excess volumes and excess surface tensions from experimental refractive indices. Phys Chem Liq. 2000;38:251–60.
46. Marcus Y. Ion solvation in nonaqueous solvents. New York: Wiley-Interscience; 1985.
47. Praveen Chand G, Gowri Sankar M, Ramachandran D, Rambabu C. Orientation effect on sign and magnitude of excess thermodynamic and transport properties of binary liquid mixtures at different temperatures. J Therm Anal Calorim. 2015;119:2069–78.
48. Yang C, Xu W, Ma P. Excess molar volumes and viscosities of binary mixtures of dimethyl carbonate with chlorobenzene, hexane, and heptane from (293.15 to 353.15) K and at Atmospheric Pressure. J Chem Eng Data. 2004;49:1802–8.
49. Nayeem Sk M, Kondaiah M, Sreekanth K, Krishna Rao D. Thermoacoustic, volumetric, and viscometric investigations in binary liquid system of cyclohexanone with benzyl benzoate at t = 30815, 31315, and 31815 K. J Thermodyn. 2014;. doi:10.1155/2014/487403.

50. Raghuram N, Suresh R, Ramesh G, Sowjanya G, Jyostna TS. Excess parameters for the binary mixtures of sulfolane with chloroethanes at different temperatures. J Therm Anal Calorim. 2015;119:2107–17.
51. Singh S, Parveen S, Shukla D, Yasmin M, Gupta M, Shukla JP. Ultrasonic and Volumetric Study of N-H Bond Complexes in Binary Mixtures. J Solut Chem. 2011;40:889–99.
52. Kermanpour F, Niakan HZ. Measurement and modeling the excess molar properties of binary mixtures of [C6mim][BF4] + 3-amino-1-propanol and {[C6mim][BF4] + isobutanol}: application of Prigogine–Flory–Patterson theory. J Chem Thermodyn. 2012;48:129–39.
53. Hartmann B. Potential energy effects on the sound speed in liquids. J Acoust Soc Am. 1979;65:1392–6.
54. Copens AB, Beyer RT, Ballou J. Parameter of nonlinearity in fluids. III. Values of sound velocity in liquid metals. J Acoust Soc Am. 1967;41:1443–8.
55. Jugan J, Khadar MA. Acoustic non-linearity parameter *B*/*A* and related molecular properties of binary organic liquid mixtures. J Mol Liq. 2002;100:217–27.
56. Dash AK, Rita P. Ultrasonic study on ternary mixture of dimethyl acetamide (DMAC) in diethyl ether and acetone. Res J Phys Sci. 2013;1:12–20.
57. Bhalodia J, Sharma S. Volumetric, refractive and FT-IR behaviour of β-pinene with o, m, p- cresol at 303.15, 308.15 and 313.15 K. J Mol Liq. 2014;193:249–55.
58. Wisniak J, Cortez G, Peralta RD, Infante R, Elizalde LE, Amaro TA, García O, Soto H. Density, excess volume, and excess coefficient of thermal expansion of the binary systems of dimethyl carbonate with butyl methacrylate, allyl methacrylate, styrene, and vinyl acetate at T = (293.15, 303.15, and 313.15) K. J Chem Thermodyn. 2008;40:1671–83.
59. Satyanarayana GR, Bala Karuna Kumar D, Sujatha K, Lakshmanarao G, Rambabu C. Probing the intermolecular interactions in the binary liquid mixtures of o-chlorophenol with alkoxyethanols through ultrasonic, transport and FTIR spectroscopic studies at different temperatures. J Mol Liq. 2016;216:526–37.