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Topological analysis of thermodynamic properties of binary mixtures containing 1-butyl-3-methylimidazolium tetrafluoroborate and cycloalkanones

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Abstract This work presents densities, ρ, speeds of sound, u, and molar heat capacities, C_p, of 1-butyl-3-methylimidazolium tetrafluoroborate (1) + cyclopentanone or cyclohexanone (2) mixtures as a function of composition at 293.15, 298.15, 303.15, 308.15 K and excess molar enthalpies, H^E of same mixtures at 298.15 K. The measured ρ, u and C_p values were used to calculate excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E and excess heat capacities, C_P^E. The V^E, κ_S^E, H^E and C_P^E have been tested in terms of Graph theory. The analysis of V^E data and IR spectroscopic data has suggested that $(1 + 2)$ mixtures are characterized by interactions between hydrogen and oxygen atom of cyclopentanone or cyclohexanone with fluorine atom of $[BF_4]^-$ anion and proton of $-CH_3$ group attached to imidazolium ring of $[Bmim]^+$ cation. The quantum mechanical calculations also support the proposed molecular entities in pure as well as mixed states along with observations inferred from IR data of the studied mixtures. The V^E, κ_S^E, H^E and C_P^E values estimated by Graph theory are in agreement with experimental values.

Keywords Connectivity parameter of third degree, $^3\xi$ · Densities, ρ · Excess molar volumes, V^E · Excess isentropic compressibilities, κ_S^E · Excess molar enthalpies, H^E · Excess heat capacities, C_P^E

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Introduction

Ionic liquids (ILs) due to their unique physical properties such as negligible vapor pressure at room temperature, wide liquid range, solvating properties for diverse substances, high thermal and chemical stability [1–4] have attracted much attention as a promising alternative to the conventional organic solvents involved in various technological and separation processes in industries processes. Due to their significant and beneficial properties, these have also been utilized in sustainable processes for organic synthesis, catalysis, extraction and separation [5–8]. These imidazolium cations-based ILs are considered to be efficient for various processes such as high absorption of carbon dioxide, diesel extractive desulfurization (EDS), oxidative desulfurization (ODS), catalytic desulfurization (ECODS) [9–12]. Over the past few years, a considerable amount of experimental data and modeling work has been reported on thermodynamic properties of imidazolium-based ILs with different alkyl groups substituted on the ring of imidazolium cation and organic solvents. Such studies have yielded positive results in the extraction of aromatic sulfur compounds. Imidazolium-based ILs containing tetrafluoroborate anion [BF_4] are considered to have good efficiency for the extraction of organic compounds and also act as good oxidizing agents [13–15]. Excess molar enthalpies, H^E, and excess heat capacities, C_P^E, data of liquid mixtures play important role to utilize them as working fluid in refrigerator, solar cells, etc. [16–19]. The knowledge of thermodynamic properties such as V^E, κ_S^E, H^E and C_P^E of imidazolium-based IL or mixture of IL with organic solvents is therefore required to utilize them for various applications in industries or to replace conventional organic solvents. Cyclopentanone and cyclohexanone are being used as solvent for polymers,

lacquers, oils, resins in the synthesis of pharmaceuticals and in cosmetic industries [20–22]. In continuation of our recent studies, focusing on thermodynamic properties of binary mixtures containing imidazolium-based cations with organic solvents, we report here densities, ρ, speeds of sound, u, molar heat capacities, C_P and excess molar enthalpies, H^E, of 1-butyl-3-methylimidazolium tetrafluoroborate (1) + cyclopentanone or cyclohexanone (2) mixtures.

Experimental

1-Butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] (Fluka, mass fraction: ≥0.988) was used without further purification. The content of water in IL was checked time to time using Karl Fischer titration and found to be less than 340 ppm [23]. Cyclopentanone (Fluka, mass fraction: 0.992) and cyclohexanone (Fluka, mass fraction: 0.994) were purified by standard methods [24]. Details of studied chemicals, their CAS number, the source, purification method, purity and analysis method are presented in Table 1. The vibrating tube densimeter and sound analyzer manufactured by Anton Paar (Model DSA 5000) with a built-in thermostat was used for the measurement of densities, ρ, and speeds of sound, u, of pure liquids and their binary mixtures [25, 26]. These measurements are based on measuring the period of oscillation of a vibrating U-shaped hollow tube filled with the liquid samples. The calibration of the equipment was done with the doubly distilled, deionized and degassed water before each series of measurements. The ρ and u values of IL and purified liquids are reported in Table 2 and also compared well with their literature values [27–40]. The mole fraction in each mixture was obtained by measuring the masses of the components of mixtures using an electric balance (Mettler AX-205 Delta) with an uncertainty of $\pm 1 \times 10^{-5}$ g. The standard uncertainty in mole fraction is $\pm 1 \times 10^{-4}$. The uncertainties of the ρ and u measurements are ± 1.2 kg m^{-3} and 0.1 m s^{-1}, respectively. Further, the uncertainty in calculated V^E values is ± 0.1 % and in temperature measurement is ± 0.01 K.

The excess molar enthalpies, H^E, of investigated mixtures and molar heat capacities, C_p, of pure liquids and their binary mixtures were measured by using micro

differential scanning calorimeter Micro DSC (Model–μDSC 7 Evo) supplied by M/S SETARAM instrumentation, France, in the manner as described elsewhere [41, 42]. The calibration of calorimeter (controlled by the software) was done by the Joule effect method and checked by measuring the heat of fusion of naphthalene 148.21 J g^{-1} which is comparable to literature value 148.7 J g^{-1} [43]. The molar heat capacities, C_p, of pure liquids are listed and compared with literature values in Table 2 [27, 30, 32, 44–47]. The uncertainties in measured C_P and H^E are ± 0.3 and ± 1 %, respectively. The uncertainty in temperature measurement is ± 0.02 K.

Results

The densities, ρ, speeds of sounds, u and molar heat capacities, C_p of [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures at 293.15, 298.15, 303.15 and 308.15 K and excess molar enthalpies, H^E at 298.15 K measured over entire composition range are listed in supplementary Tables S1, S2 and S3, respectively. The excess molar volumes, V^E, and isentropic compressibilities, κ_S, were calculated by utilizing the experimental data using the following equations:

$$V^E = \sum_{i=1}^{2} \left[\frac{x_i M_i}{\rho} - \frac{x_i M_i}{\rho_i} \right] \tag{1}$$

$$\kappa_S = \frac{1}{\rho u^2} \tag{2}$$

where x_1, x_2 are mole fractions; M_1, M_2 are molar masses and ρ_1, ρ_2 are densities of [Bmim][BF$_4$] (1) and cyclopentanone or cyclohexanone (2), respectively. The ρ and u are densities and speeds of sound values of mixtures.

The excess isentropic compressibilities, κ_S^E and excess heat capacities, C_P^E were obtained using:

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{3}$$

$$C_P^E = (C_P)_{mix} - \sum_{i=1}^{2} x_i (C_P)_i \tag{4}$$

where $(C_p)_{mix}$ denotes the molar heat capacities of the mixtures, $(C_p)_1$, $(C_p)_2$ are molar heat capacities of pure

Table 1 Details of studied chemicals, CAS registry number, their source, purification method, purity and analysis method

Chemical name	CAS number	Source	Purification method	Initial purity	Final purity	Analysis method
1-Butyl-3-methylimidazolium tetrafluoroborate	174501-65-6	Fluka	Used as such	≥0.988	–	–
Cyclopentanone	120-92-3	Fluka	Fractional distillation	0.99	0.992	GC
Cyclohexanone	108-94-1	Fluka	Fractional distillation	≥0.99	0.994	GC

GC gas chromatography

Table 2 Comparison of densities, ρ, speeds of sound, u and molar heat capacities, C_p of pure liquids with their corresponding literature values at $T = (293.15$ to $308.15)$ K

Liquids	T/K	ρ/kg m^{-3}		u/m s^{-1}		C_p/J K^{-1} mol^{-1}	
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
1-Butyl-3-methylimidazolium tetrafluoroborate	293.15	1203.1	1204.6[b]	1578.1	1578.0[d]	362.35	362.31[o]
			1204.16[c]				362.5[d]
			1202.952[d]				
	298.15	1198.9	1198.78[a]	1565.5	1565.1[d]	365.12	364.8[d]
			1199.387[d]		1565.09[a]		366.28[a]
					1566.0[e]		366.20[p]
	303.15	1195.3	1195.18[a]	1554.1	1554.0[d]	367.48	367.37[o]
			1196.98[c]		1555.5[d]		367.2[d]
			1195.818[d]		1553.15[a]		367.38[a]
	308.15	1191.7	1192.266[d]	1542.3	1542.0[d]	369.88	369.94[o]
			1191.60[a]				369.5[d]
Cyclopentanone	293.15	949.35	949.34[f]	1414.6	1414.3[f]	152.95	152.99[f]
	298.15	944.53	944.52[f]	1393.6	1393.2[f]	154.45	154.69[f]
			944.35[g]		1394.1[m]		154.5[q]
			945.30[h]				
	303.15	939.69	939.68[f]	1372.6	1372.5[f]	155.61	155.74[f]
	308.15	934.85	934.84[f]	1352.2	1352.6[f]	156.76	156.81[f]
Cyclohexanone	293.15	947.38	947.39[f]	1431.2	1430.5[n]	176.17	176.19[f]
			946.44[i]		1431.9[f]		
			947.80[j]				
	298.15	942.92	942.90[f]	1414.5	1408.0[m]	178.27	178.37[f]
			942.76[k]		1414.8[f]		177.97[r]
	303.15	938.07	938.05[f]	1395.1	1395.6[f]	180.38	180.46[f]
			940.3[l]				
	308.15	933.20	933.18[f]	1375.1	1375.8[f]	182.46	182.39[f]
			933.8[k]				

Standard uncertainties, u, are u (T) (DSA) = ±0.01 K; u (ρ) = ±1.2 kg m^{-3}; u (u) = ±0.1 m s^{-1}; u (C_p) = ±0.3 %; u (T) (DSC) = ± 0.02 K

[a] Ref. [27], [b] Ref. [28], [c] Ref. [29], [d] Ref. [30], [e] Ref. [31], [f] Ref. [32], [g] Ref. [33], [h] Ref. [34], [i] Ref. [35], [j] Ref. [36], [k] Ref. [37], [l] Ref. [38], [m] Ref. [39], [n] Ref. [40], [o] Ref. [44], [p] Ref. [45], [q] Ref. [46], [r] Ref. [47]

[Bmim][BF$_4$] (1) and cyclopentanone or cyclohexanone (2), respectively. The κ_S^{id} values were estimated using Benson and Kiyohaya relation [48]

$$\kappa_S^{id} = \sum_{i=1}^{2} \varphi_i \left[\kappa_{S,i} + \frac{Tv_i\alpha_i^2}{C_{P,i}} \right] - T \left(\sum_{i=1}^{2} x_i v_i \right) \frac{\left(\sum_{i=1}^{2} \varphi_i \alpha_i \right)^2}{\left(\sum_{i=1}^{2} x_i C_{P,i} \right)}$$

(5)

where φ_i, $\kappa_{S,i}$, v_i, α_i and $(C_P)_i$ ($i = 1$ or 2) are the volume fraction, isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity, respectively, of pure component (i) ($i = 1$ or 2). The α value for the studied liquids was calculated using density data in the manner as described elsewhere [49]. The excess molar enthalpies, H^E, values at desired compositions for (1 + 2) mixtures were provided directly by the software supplied

by the M/S SETARAM. The V^E, κ_S^E, H^E and C_P^E values of the (1 + 2) mixtures are presented in supplementary Tables S1, S2 and S3, and graphically shown in Figs. 1–4, respectively.

Thermodynamic properties V^E, κ_S^E, H^E and C_P^E were related to mole fraction of IL, x_1 by fitting with Redlich–Kister equation [50]:

$$Y^E = x_1(1 - x_1) \left[Y^{(0)} + Y^{(1)}(2x_1 - 1) + Y^{(2)}(2x_1 - 1)^2 \right]$$

(6)

where Y represents V or κ_S or H or C_P. The $Y^{n\ (n=0-2)}$ ($Y = V$ or κ_S or H or C_P) are binary adjustable parameters and were obtained by the method of least squares. The standard deviations, σ (Y^E) ($Y = V$ or κ_S or H or C_P) in Y^E ($Y = V$ or κ_S or H or C_P) were calculated using
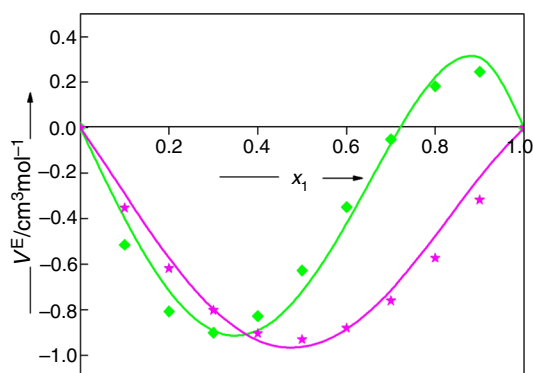
Fig. 1 Excess molar volumes, V_{12}^E for (I) [Bmim][BF$_4$] (1) + cyclopentanone (2) expt. (*green line*); graph (*green diamond*) (II) [Bmim][BF$_4$] (1) + cyclohexanone (2) expt. (*pink line*); graph (*pink star*) at 298.15 K. (Color figure online)

Fig. 2 Excess isentropic compressibilities, $\left(\kappa_S^E\right)_{12}$ for (I) [Bmim][BF$_4$] (1) + cyclopentanone (2) expt. (*green line*); graph (*green diamond*) (II) [Bmim][BF$_4$] (1) + cyclohexanone (2) expt. (*pink line*); graph (*pink star*) at 298.15 K. (Color figure online)
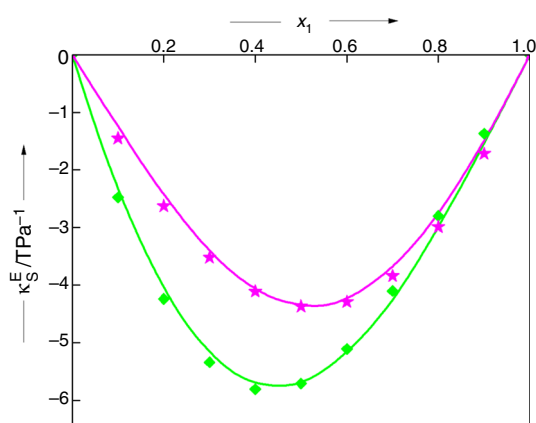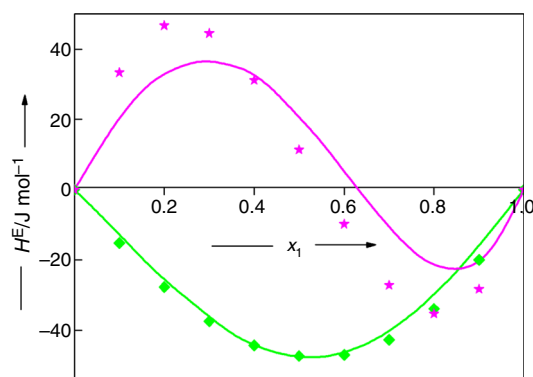

Fig. 3 Excess molar enthalpies, H_{12}^E for (I) [Bmim][BF$_4$] (1) + cyclopentanone (2) expt. (*green line*); graph (*green diamond*) (II) [Bmim][BF$_4$] (1) + cyclohexanone (2) expt. (*pink line*); graph (*pink star*) at 298.15 K. (Color figure online)

Fig. 4 Excess heat capacities, $\left(C_P^E\right)_{12}$ for (I) [Bmim][BF$_4$] (1) + cyclopentanone (2) expt. (*green line*); graph (*green diamond*) (II) [Bmim][BF$_4$] (1) + cyclohexanone (2) expt. (*pink line*); graph (*pink star*) at 298.15 K. (Color figure online)
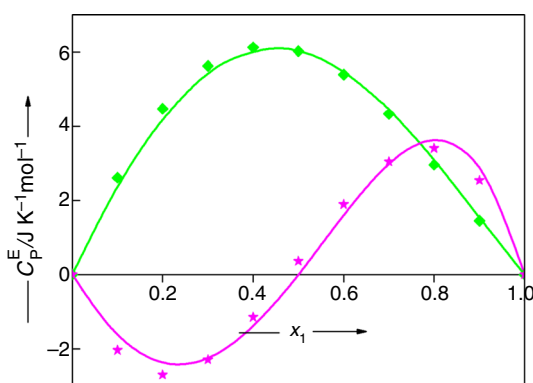
$$\sigma\left(Y^E\right) = \left\{\frac{\sum\left(Y_{(\text{expt.})}^E - Y_{\{\text{calc.equation}(6)\}}^E\right)^2}{(m-n)}\right\}^{0.5} \quad (7)$$

where m is the number of data points, n is the number of parameters in Eq. (7). The obtained binary parameters along with σ for V^E, κ_S^E, H^E and C_P^E are summarized in Table 3.

Discussion

The V^E, κ_S^E, H^E and C_P^E data of [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures are not available in the literature for comparison with experimental results. The V^E values of [Bmim][BF$_4$] (1) + cyclohexanone (2) and κ_S^E of [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures are negative across full range of composition at investigated temperatures. However, sign of V^E values changes from negative to positive with increase in concentration of [Bmim][BF$_4$] for the [Bmim][BF$_4$] (1) + cyclopentanone (2) mixture. Further, the sign and magnitude of H^E and C_P^E data of [Bmim][BF$_4$] (1) + cyclohexanone (2) mixtures are dictated by the relative proportion of components (1)/(2) in mixed state. However, for [Bmim][BF$_4$] (1) + cyclopentanone (2) mixture, while H^E values are negative; C_P^E data are positive over entire mole fraction range.

The results reported in supplementary Table S1 indicate that ρ values decrease with an increase in temperature for both the mixtures. Also the ρ values increase with increase in mole fraction of IL. The increase in ρ values with increase in concentration of IL may be due to the strengthening of interactions among IL and cyclopentanone or cyclohexanone in the mixed state. The sign and magnitude of V^E

Table 3 Binary adjustable parameters, Y^n σ (Y^E) ($Y = V$ or κ_S or H or C_P; $n = 0$–2) of Eq. (6) along with their standard deviations, σ (Y^E) ($Y = V$ or κ_S or H or C_P) of V^E, κ_S^E, C_P^E at $T = $ (293.15–308.15) K and H^E at $T = $ 298.15 K

Parameters	T/K			
	293.15	298.15	303.15	308.15
1-Butyl-3-methylimidazolium tetrafluoroborate (1) + cyclopentanone (2)				
$V^{(0)}$	−2.288	−2.882	−3.381	3.795
$V^{(1)}$	4.444	4.891	5.225	5.612
$V^{(2)}$	3.646	3.710	3.185	2.531
$\sigma(V^E)$/cm^3 mol^{-1}	0.0002	0.0004	0.0005	0.0006
$\kappa_S^{(0)}$	−20.95	−22.70	−24.54	−26.44
$\kappa_S^{(1)}$	4.79	5.43	6.03	6.56
$\kappa_S^{(2)}$	5.26	2.03	−1.00	−3.93
$\sigma(\kappa_S^E)$/TPa^{-1}	0.01	0.01	0.01	0.01
$H^{(0)}$	–	−188	–	–
$H^{(1)}$	–	−21.2	–	–
$H^{(2)}$	–	45.6	–	–
$\sigma(H^E)$/J mol^{-1}	–	0.31	–	–
$C_P^{(0)}$	22.08	24.08	26.10	28.07
$C_P^{(1)}$	−3.93	−5.74	−7.18	−8.43
$C_P^{(2)}$	−6.71	−3.88	−1.79	0.60
$\sigma(C_P^E)$/J K^{-1} mol^{-1}	0.01	0.01	0.01	0.01
1-Butyl-3-methylimidazolium tetrafluoroborate (1) + cyclohexanone (2)				
$V^{(0)}$	−3.548	−3.855	−4.236	−4.576
$V^{(1)}$	0.453	0.506	0.499	0.479
$V^{(2)}$	1.877	1.612	1.670	1.484
$\sigma(V^E)$/cm^3 mol^{-1}	0.001	0.001	0.001	0.001
$\kappa_S^{(0)}$	−15.58	−17.39	−19.41	−21.26
$\kappa_S^{(1)}$	−1.79	−1.67	−1.52	−1.25
$\kappa_S^{(2)}$	5.72	3.46	1.38	−1.02
$\sigma(\kappa_S^E)$/TPa^{-1}	0.004	0.004	0.005	0.006
$H^{(0)}$	–	83.3	–	–
$H^{(1)}$	–	−282	–	–
$H^{(2)}$	–	−130	–	–
$\sigma(H^E)$/J mol^{-1}	–	0.20	–	–
$C_P^{(0)}$	−2.30	0.01	2.24	4.39
$C_P^{(1)}$	32.01	31.17	30.52	30.44
$C_P^{(2)}$	8.50	10.84	11.91	13.50
$\sigma(C_P^E)$/J K^{-1} mol^{-1}	0.003	0.003	0.003	0.004

values is an inductive to difference in packing efficiency and interaction intensity among the constituent molecules. The negative V^E values for [Bmim][BF$_4$] (1) + cyclohexanone (2) mixture suggest a more efficient packing or attractive interactions in mixed state. The packing effect may be due to difference in molar volume (at T/K = 298.15) of [Bmim][BF$_4$] (188.52 × 10^{-6} cm^3 mol^{-1}) and cyclohexanone (104.08 × 10^{-6} cm^3 mol^{-1}) which leads to the accommodation of cyclohexanone in the interstices of IL network and hence leads to contraction in volume of mixtures. The V^E values of [Bmim][BF$_4$] (1) + cyclohexanone (2) mixture are more negative than those of [Bmim][BF$_4$] (1) + cyclopentanone (2) mixture. It may be due to reason that cyclohexanone possesses chain form with almost no strain and so can be easily accommodated in the interstices of [Bmim][BF$_4$] as compared to cyclopentanone (89.06 × 10^{-6} cm^3 mol^{-1}). Further, the comparison of V^E values of [Bmim][BF$_4$] (1) + cyclopentanone or

cyclohexanone (2) with [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) [32] has revealed that V^E values of [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) are more negative than those of corresponding [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures, thereby indicating that packing efficiency is more in mixtures containing [Emim][BF$_4$]. It may be due to larger alkyl chain attached to imidazolium ring of [Bmim]$^+$ cation which in turn restrict the approach of cyclopentanone or cyclohexanone toward [Bmim]$^+$ cation in comparison with [Emim]$^+$ cation. The $\partial V^E / \partial T$ and $\partial (\kappa_S^E) / \partial T$ for the present mixtures are negative which suggest strong interactions exist among the unlike molecules in the mixtures. This is also supported by decrease in speeds of sound values with increase in temperature, also suggesting strong interactions between the components of the mixtures.

The sign and magnitude of H^E values of liquid mixtures reflects the interactions between like and unlike molecules. The positive H^E data suggest that interactions between unlike molecules are weaker than between like molecules, whereas negative H^E data view to the opposite. The H^E of present (1 + 2) mixtures may be explained, if we assume that (i) [Bmim][BF$_4$] is characterized by cohesion forces and exist as monomer; cyclopentanone or cyclohexanone are characterized by dipole–dipole interactions and exist as associated entities; (ii) addition of (1) to (2) or vice versa ruptures cohesion forces in [Bmim][BF$_4$] and dipole–dipole interactions in cyclopentanone or cyclohexanone to give (1) and (2) molecules; and (iii) (1) and (2) molecules undergo interactions to form 1:2 molecular complex. The negative H^E values of [Bmim][BF$_4$] (1) + cyclopentanone (2) mixtures indicate that contribution to H^E due to factor (iii) is more than due to factor (ii). However, positive H^E data of [Bmim][BF$_4$] (1) + cyclohexanone (2) at $x_1 \leq 0.6315$ suggest that contribution to H^E due to destruction of cohesive forces in IL or dipole–dipole interactions in cyclopentanone is higher in comparison with like molecule interaction. However, at $x_1 > 0.6315$ the unlike interactions dominate over like interactions. Cyclohexanone is more basic in character than cyclopentanone and also possesses chain form with no strain. Consequently, cyclohexanone must interact strongly with [Bmim][BF$_4$] in comparison with cyclopentanone. Thus, H^E for [Bmim][BF$_4$] (1) + cyclohexanone (2) mixture should be less than those for [Bmim][BF$_4$] (1) + cyclopentanone (2) mixture. This is not true. It may be due to fact that cyclohexanone is larger in size than cyclopentanone and so requires more energy to break cohesion forces in [Bmim][BF$_4$]. The H^E values of [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures have been reported in the literature [32]. The comparison of H^E data for [Bmim][BF$_4$] or [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures has revealed that H^E values for

[Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures are lesser than [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures. It may be due to larger alkyl chain attached to imidazolium ring of [Bmim]$^+$ cation which in turn restrict the approach of cyclopentanone or cyclohexanone molecules toward [Bmim]$^+$ in comparison with [Emim]$^+$.

The positive C_P^E values for [Bmim][BF$_4$] (1) + cyclopentanone (2) mixture suggest that contribution to C_P^E due to formation of 1:2 molecular complex (possessing non-random structure) dominate over contribution due to rupture of cohesion forces in IL and dipole–dipole interactions in cyclopentanone. Further, for [Bmim][BF$_4$] (1) + cyclohexanone (2) mixture, C_P^E values are both positive and negative. The negative C_P^E values at $x_1 \leq 0.5352$ suggest that contribution to C_P^E due to complexity among constituent molecules is less than contribution due to rupture of cohesion forces in IL and dipole–dipole interactions in cyclohexanone. However, positive C_P^E values indicate the domination of C_P^E due to formation of 1:2 molecular complex possessing non-random structure. The $\partial (C_P^E) / \partial T$ for the studied mixtures are positive. This may be due to the destructions of associated molecular entities cyclopentanone or cyclohexanone and ionic interactions in IL which suggests that the interactions between like molecules are more difficult than between unlike molecules which in turn leads to more packed structure in mixed state.

The V^E, κ_S^E, H^E and C_P^E data for the present mixtures were next analyzed in terms of Graph theory.

Graph theory

Graph theory has been utilized [51–54] successfully to obtain information about state of components in pure and mixed state along with nature and extent of interaction existing in mixtures. The theory involves the topology of the constituent molecules which in turn is described by connectivity parameters of third degree of a molecule, $^3\xi$. As the topology of the constituent molecules in pure state changes in mixed state and excess molar volumes, V^E reflects packing effect, the V^E data of (1 + 2) mixtures were analyzed in terms of Graph theory. According to Graph theory [55, 56], excess molar volumes, V^E, is given by

$$V^E = \alpha_{12} \left[\frac{1}{\sum_{i=1}^{2} x_i (^3\xi_i)_m} - \frac{x_1}{^3\xi_1} - \frac{x_2}{^3\xi_2} \right] \quad (8)$$

where x_1 is the mole fraction of IL and α_{12} is a constant characteristic of (1 + 2) mixtures. The α_{12} parameter for the present mixtures has been determined by employing V^E

values at $x_1 = 0.6$. The $(^3\xi_i)$ ($i = 1$ or 2); $(^3\xi_i)_m$ ($i = 1$ or 2) are connectivity parameters of third degree of 1/2 molecule and are defined by

$$^3\xi = \sum_{m<n<o<p} \left(\delta_m^v \delta_n^v \delta_o^v \delta_p^v \right)^{-0.5} \qquad (9)$$

where δ_m^v, etc. is related to the maximum valency, Z_m, and number of hydrogen atoms, h, attached to mth vertex by relation: $\delta^v = Z_m - h$ [57]. The $(^3\xi_i)$ ($i = 1$ or 2), $(^3\xi_i)_m$ ($i = 1$ or 2) values were determined by employing V^E data of $(1 + 2)$ mixtures to Eq. (8) and only those values were considered that yielded V^E values comparable to experimental data. Such V^E values along with experimental values, $(^3\xi_i)$ ($i = 1$ or 2); $(^3\xi_i)_m$ ($i = 1$ or 2), α_{12} parameters for the investigated mixtures are recorded in Tables 4, 5, respectively. Examination of Table 4 has indicated that V^E values for [Bmim][BF$_4$] (1) + cyclohexanone (2) mixture are comparable with experimental values. Also V^E values for [Bmim][BF$_4$] (1) + cyclopentanone (2) mixture compare well at $x_1 \leq 0.6942$. The failure of theory to correctly predict V^E data at $x_1 > 0.6942$ is due to estimation of α_{12} parameter by employing V^E values at one composition.

A number of structures were then assumed for [Bmim][BF$_4$], cyclopenanone and cyclohexanone. Structure or combination of structures providing $(^3\xi')$ values (using

structural consideration, i.e., Eq. 9) closest to $(^3\xi)$ values (determined via Eq. 8) was taken to be representative structure of [Bmim][BF$_4$], cyclopenanone and cyclohexanone. It was assumed that [Bmim][BF$_4$], cyclopenanone and cyclohexanone exist as molecular entities I, II–IV and V–VII, respectively. The $(^3\xi')$ values for these molecular entities were found to be 2.698, 0.984, 1.347, 1.386, 1.411, 1.597, 1.935, respectively (Scheme 1). In evaluating $(^3\xi')$ for [Bmim][BF$_4$], it was assumed that cohesion forces exist between (1) hydrogen atom of C–H (edge) of imidazolium ring and two fluorine atoms of [BF$_4$]$^-$; (2) proton of –CH$_3$ group of imidazolium ring and fluorine atom of [BF$_4$]$^-$. Since [Bmim][BF$_4$] has $(^3\xi)$ value of 2.396 (Table 5), the present analysis revealed that [Bmim][BF$_4$] exists as molecular entity I. Further, $(^3\xi)$ values of 1.287 and 2.105 for cyclopentanone and cyclohexanone (Table 5) suggest that cyclopentanone and cyclohexanone exist as a mixture of open and cyclic dimers. The $(^3\xi'_1)_m$ were then estimated to obtain information about the state of [Bmim][BF$_4$] in cyclopentanone and cyclohexanone. We assumed that present $(1 + 2)$ mixtures may contain molecular entities VIII–IX which in turn are characterized by interactions between hydrogen and oxygen atoms of cyclopentanone or cyclohexanone with fluorine atom of [BF$_4$]$^-$ anion and proton of methyl group attached to imidazolium ring of [Bmim]$^+$ cation. The $(^3\xi'_1)_m$ value for

Table 4 Comparison of measured V^E, κ_S^E, C_P^E values from appropriate equations with their corresponding experimental values at $T = (293.15\text{--}308.15)$ K and H^E at $T = 298.15$ K

Properties	Mole fraction of component (1), x_1								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1-Butyl-3-methylimidazolium tetrafluoroborate (1) + cyclopentanone (2)									
$T/K = 293.15$									
V^E (expt.)/cm^3 mol^{-1}	−0.321	−0.569	−0.732	−0.731	−0.583	−0.321	0.032	0.279	0.321
V^E (graph)$_{\text{Eq.15}}$/cm^3 mol^{-1}	−0.430	−0.666	−0.732	−0.656	−0.471	−0.224	0.032	0.223	0.255
κ_S^E (expt.)/TPa^{-1}	−1.91	−3.51	−4.72	−5.29	−5.30	−4.69	−3.71	−2.52	−1.30
κ_S^E (graph)/TPa^{-1}	−2.24	−3.85	−4.85	−5.29	−5.22	−4.69	−3.79	−2.61	−1.29
C_P^E (expt.)/J K^{-1} mol^{-1}	1.81	3.59	4.92	5.61	5.53	4.91	3.90	2.72	1.41
C_P^E (graph)/J K^{-1} mol^{-1}	2.40	4.11	5.17	5.61	5.50	4.91	3.93	2.67	1.29
$T/K = 298.15$									
V^E (expt.)/cm^3 mol^{-1}	−0.404	−0.704	−0.901	−0.890	−0.732	−0.421	−0.052	0.229	0.293
V^E (graph)$_{\text{Eq.15}}$/cm^3 mol^{-1}	−0.515	−0.807	−0.901	−0.828	−0.628	−0.349	−0.052	0.182	0.246
κ_S^E (expt.)/TPa^{-1}	−2.29	−4.03	−5.19	−5.81	−5.82	−5.11	−4.12	−2.90	−1.59
κ_S^E (graph)/TPa^{-1}	−2.48	−4.24	−5.34	−5.81	−5.71	−5.11	−4.10	−2.80	−1.37
H^E (expt.)/J mol^{-1}	−13.2	−25.1	−36.4	−44.3	−48.9	−47.0	−40.1	−28.8	−15.9
H^E (graph)/J mol^{-1}	−15.2	−27.7	−37.4	−44.3	−47.3	−47.0	−42.7	−33.9	−20.0
C_P^E (expt.)/J K^{-1} mol^{-1}	2.30	4.22	5.61	6.12	6.04	5.39	4.32	3.05	1.60
C_P^E (graph)/J K^{-1} mol^{-1}	2.61	4.47	5.62	6.12	6.02	5.39	4.33	2.96	1.45
$T/K = 303.15$									
V^E (expt.)/cm^3 mol^{-1}	−0.490	−0.871	−1.052	−1.041	−0.849	−0.511	−0.158	0.151	0.252

Table 4 continued

Properties	Mole fraction of component (1), x_1								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
V^E (graph)$_{Eq.15}$/cm^3 mol^{-1}	−0.587	−0.928	−1.052	−0.990	−0.784	−0.485	−0.158	0.112	0.215
κ_S^E (expt.)/TPa^{-1}	−2.70	−4.50	−5.71	−6.31	−6.32	−5.60	−4.49	−3.31	−1.91
κ_S^E (graph)/TPa^{-1}	−2.67	−4.58	−5.78	−6.31	−6.23	−5.60	−4.53	−3.12	−1.54
C_P^E (expt.)/J K^{-1} mol^{-1}	2.72	4.81	6.20	6.69	6.51	5.82	4.71	3.30	1.81
C_P^E (graph)/J K^{-1} mol^{-1}	2.88	4.92	6.17	6.69	6.54	5.82	4.63	3.13	1.50
T/K = 308.15									
V^E (expt.)/cm^3 mol^{-1}	−0.601	−1.004	−1.178	−1.162	−0.961	−0.603	−0.241	0.072	0.209
V^E (graph)$_{Eq.15}$/cm^3 mol^{-1}	−0.647	−1.031	−1.178	−1.124	−0.912	−0.595	−0.241	0.061	0.193
κ_S^E (expt.)/TPa^{-1}	−3.11	−5.02	−6.22	−6.79	−6.80	−6.11	−5.03	−3.70	−2.22
κ_S^E (graph)/TPa^{-1}	−2.84	−4.89	−6.19	−6.79	−6.74	−6.11	−4.99	−3.49	−1.76
C_P^E (expt.)/J K^{-1} mol^{-1}	3.11	5.43	6.79	7.20	7.05	6.21	5.13	3.69	2.02
C_P^E (graph)/J K^{-1} mol^{-1}	3.12	5.33	6.66	7.20	7.02	6.21	4.91	3.29	1.55
1-Butyl-3-methylimidazolium tetrafluoroborate (1) + cyclohexanone (2)									
T/K = 293.15									
V^E (expt.)/cm^3 mol^{-1}	−0.242	−0.503	−0.732	−0.871	−0.910	−0.804	−0.621	−0.402	−0.190
V^E (graph)$_{Eq.8}$/cm^3 mol^{-1}	−0.322	−0.565	−0.732	−0.825	−0.848	−0.804	−0.695	−0.523	−0.290
κ_S^E (expt.)/TPa^{-1}	−1.04	−1.90	−2.81	−3.59	−4.03	−3.92	−3.22	−2.30	−1.21
κ_S^E (graph)/TPa^{-1}	−1.17	−2.18	−3.00	−3.59	−3.91	−3.92	−3.58	−2.85	−1.67
C_P^E (expt.)/J K^{-1} mol^{-1}	−2.11	−3.03	−2.90	−2.02	−0.50	1.12	2.58	3.09	2.21
C_P^E (graph)/J K^{-1} mol^{-1}	−2.33	−3.19	−2.90	−1.81	−0.27	1.32	2.58	3.08	2.38
T/K = 298.15									
V^E (expt.)/cm^3 mol^{-1}	−0.290	−0.561	−0.811	−0.949	−0.982	−0.881	−0.704	−0.451	−0.232
V^E (graph)$_{Eq.8}$/cm^3 mol^{-1}	−0.353	−0.619	−0.802	−0.904	−0.930	−0.881	−0.761	−0.573	−0.318
κ_S^E (expt.)/TPa^{-1}	−1.31	−2.29	−3.30	−4.11	−4.52	−4.29	−3.61	−2.69	−1.50
κ_S^E (graph)/TPa^{-1}	−1.45	−2.63	−3.52	−4.11	−4.37	−4.29	−3.84	−2.99	−1.72
H^E (expt.)/J mol^{-1}	17.4	34.2	44.5	45.0	32.1	−8.02	−27.2	−26.8	−15.0
H^E (graph)/J mol^{-1}	33.3	46.7	44.5	31.2	11.4	−9.79	−27.2	−35.3	−28.3
C_P^E (expt.)/J K^{-1} mol^{-1}	−1.69	−2.52	−2.29	−1.41	0.14	1.71	3.04	3.50	2.52
C_P^E (graph)/J K^{-1} mol^{-1}	−2.04	−2.70	−2.29	−1.15	0.36	1.89	3.04	3.40	2.54
T/K = 303.15									
V^E (expt.)/cm^3 mol^{-1}	−0.321	−0.622	−0.889	−1.032	−1.071	−0.982	−0.782	−0.511	−0.259
V^E (graph)$_{Eq.8}$/cm^3 mol^{-1}	−0.393	−0.690	−0.894	−1.008	−1.036	−0.982	−0.848	−0.638	−0.355
κ_S^E (expt.)/TPa^{-1}	−1.62	−2.80	−3.79	−4.62	−5.02	−4.80	−4.12	−3.11	−1.79
κ_S^E (graph)/TPa^{-1}	−1.64	−2.97	−3.97	−4.62	−4.91	−4.80	−4.28	−3.33	−1.91
C_P^E (expt.)/J K^{-1} mol^{-1}	−1.32	−1.95	−1.72	−0.59	0.71	2.19	3.45	3.89	2.81
C_P^E (graph)/J K^{-1} mol^{-1}	−1.76	−2.23	−1.72	−0.55	0.95	2.41	3.45	3.68	2.68
T/K = 308.15									
V^E (expt.)/cm^3 mol^{-1}	−0.363	−0.679	−0.970	−1.121	−1.153	−1.063	−0.851	−0.590	−0.304
V^E (graph)$_{Eq.8}$/cm^3 mol^{-1}	−0.426	−0.747	−0.967	−1.091	−1.122	−1.063	−0.918	−0.691	−0.384
κ_S^E (expt.)/TPa^{-1}	−1.90	−3.31	−4.32	−5.08	−5.50	−5.21	−4.50	−3.52	−2.09
κ_S^E (graph)/TPa^{-1}	−1.84	−3.30	−4.39	−5.08	−5.36	−5.21	−4.62	−3.56	−2.03
C_P^E (expt.)/J K^{-1} mol^{-1}	−1.04	−1.51	−1.14	0.05	1.32	2.70	3.89	4.28	3.10
C_P^E (graph)/J K^{-1} mol^{-1}	−1.49	−1.77	−1.14	0.08	1.56	2.95	3.89	3.99	2.83

Table 5 Interaction energies parameters, χ'_{12}, χ^* and α_{12} along with connectivity parameters of third degree of a molecule, $(^3\xi_i)$ and $(^3\xi_i)_m$ ($i = 1$ or 2) utilized in Graph theory for the determination of V^E, κ_S^E and C_P^E at $T = (293.15–308.15)$ K and H^E at $T = 298.15$ K. Also included are the deviations, $\sigma(V^E_{\text{graph}})$, $\sigma(\kappa_{S\ \text{graph}}^E)$, $\sigma(H^E_{\text{graph}})$ and $\sigma(C_{P\ \text{graph}}^E)$ between the experimental values and values obtained from Graph theory

Parameters	T/K			
	293.15	298.15	303.15	308.15
1-Butyl-3-methylimidazolium tetrafluoroborate (1) + cyclopentanone (2)				
$(^3\xi_1) = (^3\xi_1)_m$	2.396	2.396	2.396	2.396
$(^3\xi_2) = (^3\xi_2)_m$	1.287	1.287	1.287	1.287
$\chi_{12}^{\prime v}$/cm^3 mol^{-1}	−2.665	−3.170	−3.584	−3.936
χ^{*v}/cm^3 mol^{-1}	2.548	2.824	2.965	3.101
$\sigma(V^E_{\text{graph}})$	0.090	0.082	0.057	0.032
$\chi_{12}^{\prime \kappa}$/TPa^{-1}	−12.83	−14.21	−15.28	−16.19
$\chi^{*\kappa}$/TPa^{-1}	3.20	3.76	3.79	3.57
$\sigma(\kappa_{S\ \text{graph}}^E)$	0.19	0.16	0.17	0.22
$\chi_{12}^{\prime H}$/J mol^{-1}	–	−84.2	–	–
χ^{*H}/J mol^{-1}	–	−19.7	–	–
$\sigma(H^E_{\text{graph}})$	–	31.4	–	–
$\chi_{12}^{\prime C_P}$/J K^{-1} mol^{-1}	13.79	14.95	16.56	17.98
χ^{*C_P}/J K^{-1} mol^{-1}	−3.78	−3.92	−4.72	−5.40
$\sigma(C_{P\ \text{graph}}^E)$	0.32	0.17	0.16	0.26
1-Butyl-3-methylimidazolium tetrafluoroborate (1) + cyclohexanone (2)				
$(^3\xi_1) = (^3\xi_1)_m$	2.396	2.396	2.396	2.396
$(^3\xi_2) = (^3\xi_2)_m$	2.105	2.105	2.105	2.105
α_{12}/cm^3 mol^{-1}	454.838	498.398	555.536	601.359
$\sigma(V^E_{\text{graph}})$	0.081	0.073	0.077	0.067
$\chi_{12}^{\prime \kappa}$/TPa^{-1}	−6.20	−7.87	−8.93	−10.08
$\chi^{*\kappa}$/TPa^{-1}	−5.38	−4.63	−5.03	−5.01
$\sigma(\kappa_{S\ \text{graph}}^E)$	0.34	0.24	0.15	0.08
$\chi_{12}^{\prime H}$/J mol^{-1}	–	223	–	–
χ^{*H}/J mol^{-1}	–	−292	–	–
$\sigma(H^E_{\text{graph}})$	–	13.5	–	–
$\chi_{12}^{\prime C_P}$/J K^{-1} mol^{-1}	−15.86	−14.16	−12.54	−10.93
χ^{*C_P}/J K^{-1} mol^{-1}	22.76	22.61	22.38	22.26
$\sigma(C_{P\ \text{graph}}^E)$	0.19	0.21	0.25	0.28

these molecular entities was then calculated to be 2.358. The $(^3\xi_1)_m$ value of 2.396 (Table 5) suggest the presence of molecular entities VIII–IX in [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures.

The existence of molecular entities VIII–IX in the present (1 + 2) mixtures advocated that addition of cyclopentanone or cyclohexanone to [Bmim][BF$_4$] must influence (i) C–H vibrations of [Bmim]$^+$ cation; (ii) B–F stretching of [BF$_4$]$^-$ anion; (iii) in plane bending vibrations of –CH$_3$ group in [Bmim][BF$_4$]; and (iv) > C=O vibrations of cyclopentanone or cyclohexanone. The IR studies of pure [Bmim][BF$_4$], cyclopentanone, cyclohexanone and their equimolar (1 + 2) mixtures has revealed that [Bmim][BF$_4$], cyclopentanone, cyclohexanone exhibited characteristic vibrations [27, 58–60] at 3156 cm^{-1} (C–H vibrations); 528 cm^{-1} (B–F stretching); 1042 cm^{-1} (in plane bending vibrations of –CH$_3$); and 1730, 1720 cm^{-1} (>C=O vibrations of cyclopentanone or cyclohexanone) which were shifted to 3154, 3150 cm^{-1} (C–H vibrations); 520, 522 cm^{-1} (B–F stretching); 1057, 1060 cm^{-1} (in plane bending vibrations of –CH$_3$); and 1716, 1708 cm^{-1} (>C=O vibrations of cyclopentanone or cyclohexanone). The IR studies thus lend additional support to the postulation of molecular entities VIII–IX in the mixed state.

The postulation of molecular entities I–VII in pure and VIII–IX in mixed states was further confirmed by

predicting inter-nuclear distances between the interacting atoms of the components of mixtures by quantum mechanics calculations using density functional theory [61–63]. All quantum mechanical calculations were performed with Gaussian program package 09 [64].

The full optimization of structures of [Bmim][BF$_4$], cyclopentanone, cyclohexanone (molecular entities I–VII) and their mixtures (molecular entities VIII–IX) was carried out on the B3LYP/6-311++G (d, p) level of theory [64, 65]. The various inter-nuclear distances between interacting atoms in pure [Bmim][BF$_4$], cyclopentanone, cyclohexanone and their mixed state (molecular entities I–IX) are labeled in Scheme 1. The inter-nuclear distances between hydrogen and fluorine atoms (2.28–2.96 Å) in pure [Bmim][BF$_4$] (molecular entity I) suggest interactions between protons of carbon (C2 in imidazolium ring) and –CH$_3$ group attached to imidazolium ring of [Bmim]$^+$ cation with fluorine atoms of [BF$_4$]$^-$. Also inter-nuclear distances of 3.16 and 3.19 Å between carbon and oxygen atoms of cyclopentanone (molecular entities II–IV); and cyclohexanone (molecular entities V–VII), respectively, indicate the presence of open and cyclic dimer. It has also been observed in molecular entities VIII–IX that inter-nuclear distances between the proton of –CH$_3$ group attached to imidazolium ring of [Bmim][BF$_4$] and oxygen atom of cyclopentanone or cyclohexanone are 2.84 and 2.83 Å, respectively, and inter-nuclear distances between proton of cyclopentanone or cyclohexanone and fluorine atom of [BF$_4$]$^-$ are 3.67 and 2.92 Å. Such inter-nuclear distances between interacting atoms support (i) proposed molecular entities I–IX in pure and mixed states; (ii) assumptions made for the estimation of connectivity parameters of third degree, $^3\xi'$, (via structural consideration) of molecular entities I–IX; and (iii) observations inferred from the analysis of IR spectral data of the present mixtures.

Excess molar volumes, excess isentropic compressibilities, excess molar enthalpies and excess heat capacities

The estimated V^E data for [Bmim][BF$_4$] (1) + cyclopentanone (2) mixtures (by Graph theory) are not comparable well with experimental results at $x_1 > 0.6942$. It was, therefore, worthwhile to analyze V^E data of [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures using Moelwyn–Huggins concept along with topology of the constituent molecules [66, 67]. The κ_S^E, H^E and C_P^E data of the investigated mixtures were also tested in terms of Graph theory by taking into consideration the various processes involved in the mixture formation. The analysis of V^E data in terms of Graph theory has suggested that [Bmim][BF$_4$] is characterized by cohesion forces and exists
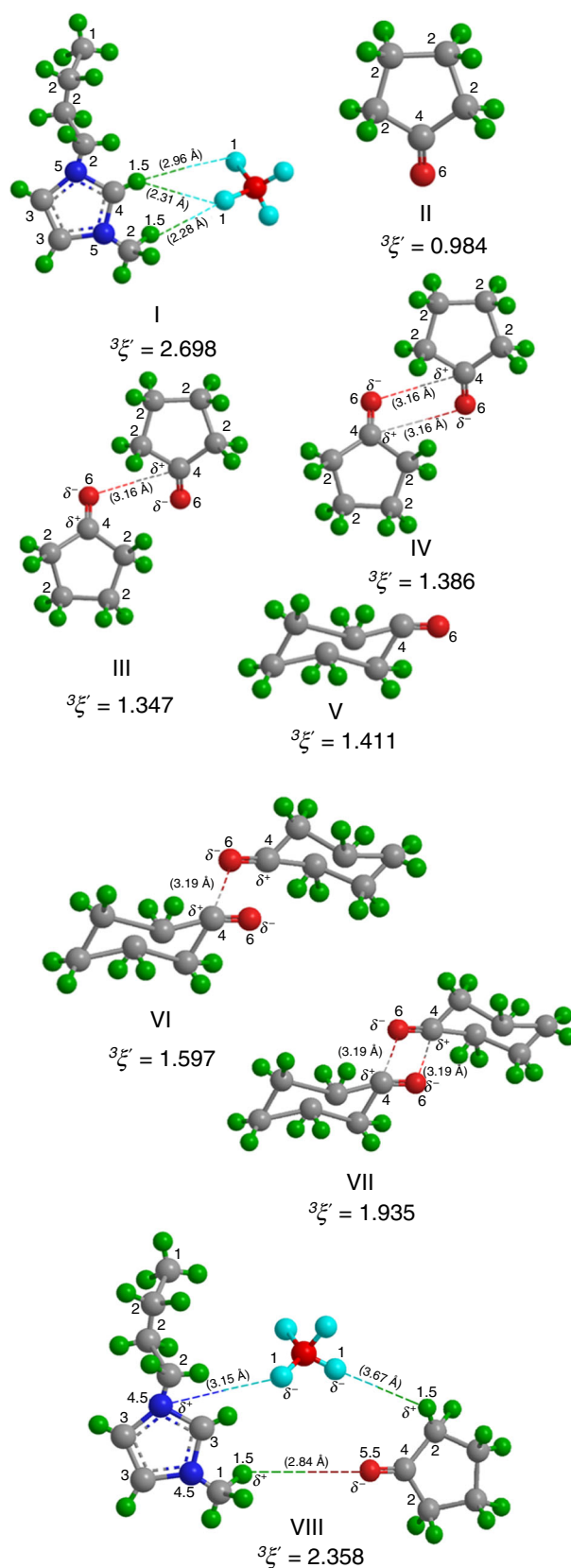
Scheme 1 Connectivity parameters, $^3\xi'$ of the third degree for various molecular entities

IX

$^3\xi' = 2.358$

● Carbon ● Hydrogen ● Boron ● Fluorine ● Nitrogen ● Oxygen
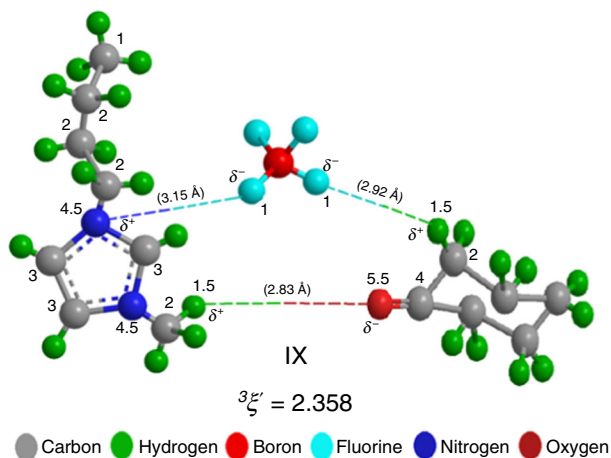
Scheme 1 continued

as monomer; cyclopentanone and cyclohexanone exist as dimer. The studies of $(1 + 2)$ mixtures formation were then assumed to involve processes; (i) formation of unlike $1\text{–}2_n$ contacts; (ii) unlike contact formation leads to rupture of cohesion forces in [Bmim][BF$_4$] as well as $2_n\text{–}2_n$ dipole interactions and results into depolymerization of 2_n to form monomer which in turn enhance randomness; (iii) monomers of (1) and (2) molecules then undergo ion–dipole interactions to form 1:2 molecular complex possessing non-random structure. If χ_{12}, χ_1, χ_2, χ_{12}^* are molar volumes, molar compressibilities, molar interaction parameters for establishment of 1–2 contacts; rupture of cohesion forces in IL and $2_n\text{–}2_n$ dipole interactions and increase in randomness; and molecular interactions between (1) and (2) to form 1:2 molecular complex; and increase in non-randomness, respectively; then change in thermodynamic properties, ΔY ($Y = V$ or κ_S or H or C_P) due to processes (i–iii) were expressed [68–70] by

$$\Delta Y_i(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P) = \left[\frac{x_1 x_2 v_2}{\sum x_1 v_1}\right][\chi_{12}] \quad (10)$$

$$\Delta Y_{ii}(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P) = \left[\frac{x_1^2 x_2 v_2}{\sum x_1 v_1}\right][\chi_1 + \chi_2] \quad (11)$$

$$\Delta Y_{iii}(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P) = \left[\frac{x_1 x_2^2 v_2}{\sum x_1 v_1}\right][\chi_{12}^*] \quad (12)$$

The overall change in the thermodynamic properties $Y^E(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P)$ for the investigated $(1 + 2)$ mixtures was then expressed by

$$Y^E(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P) = \sum_{i=i}^{iii}(\Delta Y_i)$$
$$= \left[\frac{x_1 x_2 v_2}{\sum x_1 v_1}\right][\chi_{12} + x_1 \chi_1 + x_1 \chi_2 + x_2 \chi_{12}^*] \quad (13)$$

Since $v_2/v_2 = (^3\xi_1/^3\xi_2)$ [71], Eq. (13) was expressed as

$$Y^E(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P) = \sum_{i=i}^{iii}(\Delta Y_i)$$
$$= \left[\frac{x_1 x_2(^3\xi_1/^3\xi_2)}{x_1 + x_2(^3\xi_1/^3\xi_2)}\right][\chi_{12} + x_1\chi_1 + x_1\chi_2 + x_2\chi_{12}^*] \quad (14)$$

It was, further, assumed that interaction energy parameters for the establishment of unlike contacts and formation of 1:2 molecular complex; rupture of cohesion forces in IL and dipole–dipole interactions among cycloalkanones are nearly equal, i.e., $\chi_{12} \cong \chi_{12}^* = \chi_{12}'$ and $\chi_1 \cong \chi_2 = \chi^*$, respectively; Eq. (14) was then reduced to

$$Y^E(Y = V \text{ or } \kappa_S \text{ or } H \text{ or } C_P)$$
$$= \left[\frac{x_1 x_2(^3\xi_1/^3\xi_2)}{x_1 + x_2(^3\xi_1/^3\xi_2)}\right][(1 + x_2)\chi_{12}' + 2x_1\chi^*] \quad (15)$$

Equation (15) contains two unknown parameters χ_{ij}' and χ^*. These parameters were evaluated by using experimental data of V^E, κ_S^E, H^E and C_P^E at two compositions. The estimated parameters were then utilized to predict V^E, κ_S^E, H^E and C_P^E values at other mole fractions of x_1. The V^E, κ_S^E, H^E and C_P^E values along with $\chi_{12}'^v$, χ^{*v}; $\chi_{12}'^\kappa$, $\chi^{*\kappa}$; $\chi_{12}'^H$, χ^{*H}, $\chi_{12}'^{C_P}$, χ^{*C_P} parameters are reported in Tables 4, 5, respectively, and are compared with experimental values.

Examination of data in Table 4 has indicated that V^E, κ_S^E, H^E and C_P^E values estimated by Graph theory are in agreement with experimental results. The comparison between calculated and experimental values provides additional support to the assumptions made in deriving Eq. (15). Further, V^E values for mixtures changing sign with relative proportion of the constituent molecules can be estimated during Graph theory.

Conclusions

The paper reports a new experimental data of excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E, excess heat capacities, C_P^E (at 293.15, 298.15, 303.15, 308.15 K), and excess molar enthalpies, H^E (at 298.15 K), for [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures. The V^E, κ_S^E, H^E and C_P^E were fitted to Redlich–Kister equation to determine binary adjustable parameters and standard deviations. The analyses of V^E data in terms of Graph theory suggest that while [Bmim][BF$_4$] exist as monomer; cyclopentanone and cyclohexanone exist as mixture of cyclic and open dimer. Further, $(1 + 2)$ mixtures are characterized by interactions between hydrogen and oxygen atoms of cyclopentanone or cyclohexanone with

fluorine atom of $[BF_4]^-$ anion and proton of $-CH_3$ group attached to imidazolium ring of $[Bmim]^+$ cation. The proposed molecular entities in pure and mixed state were utilized to estimate their connectivity parameters, $^3\zeta'$ which in turn were used to determine V^E, κ_S^E, H^E and C_P^E data. The quantum mechanical calculations and IR spectral data of the investigated mixtures also supported the presence of proposed molecular entities in the mixtures. It has been observed that estimated V^E, κ_S^E, H^E and C_P^E values by Graph theory compare well with their corresponding experimental values.

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