



# Excess molar enthalpies for [Bmmim][BF<sub>4</sub>] + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] + cyclopentanone or cyclohexanone mixtures

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## Abstract

In recent years, studies on mixtures consisting of ionic liquids and organic solvents have gained importance for the application of such mixtures for new chemical processes and technologies in industries. In this contribution, new experimental excess molar enthalpies,  $H_{ijk}^E$  data of ternary 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [Bmmim][BF<sub>4</sub>] (*i*) + 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF<sub>4</sub>] or 1-ethyl-3-methylimidazolium tetrafluoroborate, [Emim][BF<sub>4</sub>] (*j*) + cyclopentanone (CPO) or cyclohexanone (CHO) (*k*) mixtures, have been reported over the whole composition range at 298.15 K and atmospheric pressure. The observed data have been satisfactorily correlated by Redlich–Kister equation for each mixture. The  $H_{ijk}^E$  values for [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (*j*) + CPO (*k*) mixtures are positive over whole range of composition of  $x_i$  and  $x_j$ . The sign and magnitude of  $H_{ijk}^E$  values for [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (*j*) + CHO (*k*) mixtures vary with the change in composition of the components of the mixtures. The  $H_{ijk}^E$  data have also been analyzed in terms of graph theory (which involves the topology of the molecule). It has been observed that estimated values by graph theory compare well with their corresponding experimental values.

**Keywords** Excess molar enthalpies · Graph theory · Connectivity parameters of third degree · Interaction parameters · Ionic liquids

## Introduction

Ionic liquids (ILs) generally exhibit peculiar properties [1–4] such as broad electrochemical window, negligible vapor pressure, low melting points, low toxicity, non-flammability, high ionic conductivity, air- and water-stable behavior, wide liquid range, excellent solubility, non-volatility, recyclability, reusability, high thermal and electrochemical stability and good selectivity which are considered to be excellent fluids for use in a wide range of engineering and material applications such as chemical reactions [5], chemical extractive processes [6], electrochemistry [7], multiphase bioprocess operations [8], liquid–liquid separations [9], batteries and fuel cells [10],

synthesis [11], heat transfer fluids in solar heating and absorption refrigerating systems [12]. However, a number of engineering parameters need to be determined for the ILs or their mixtures with organic solvents in order to access their applicability to material applications and process design. Thermodynamic properties of liquid mixtures are required for the various heat flow, mass transfer, heat transfer calculations, and for designing, optimization and simulation of various industrial processes [13–16]. In particular, excess molar enthalpies,  $H^E$ , data are essential for the design of chemical reactors and heat transfer systems, which involve mixture/s comprised of ILs or their mixture with organic solvents.

ILs: 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [Bmmim][BF<sub>4</sub>], 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF<sub>4</sub>], 1-ethyl-3-methylimidazolium tetrafluoroborate, [Emim][BF<sub>4</sub>], have shown a substantial potential for many technological applications improving operational safety in many systematic processes [17], in

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bioreactor technology and in nanotechnology [18, 19]. Cyclic ketones are further important intermediates in the synthesis of many organic compounds such as alkoxides, phosphine oxides, used to create fragrances, in chewing gum, in polymers, cosmetic and pharmaceutical industries [20–23]. A literature survey has revealed that  $H^E$  values of liquid mixtures containing ILs and organic solvents can be used in variety of applications such as extractive desulfurization of liquid fuels and electrochemical capacitors [24–26].

In recent studies [27, 28], we have measured excess properties (excess molar volumes,  $V^E$ , excess isentropic compressibilities,  $\kappa_S^E$ , excess molar enthalpies,  $H^E$ , and excess heat capacities ( $C_p^E$ ) of the binary mixtures containing ILs: [Bmmim][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>], [Emim][BF<sub>4</sub>] and cycloalkanone. The measured data have been successfully analyzed in terms of graph theory which in turn deals with the topology of a molecule. This paper continues our investigations on mixtures comprised of [Bm-mim][BF<sub>4</sub>] or [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] or cycloalkanone and reports excess molar enthalpies,  $H_{ijk}^E$  data of ternary [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (*j*) + cyclopentanone (CPO) or cyclohexanone (CHO) (*k*) mixtures over the entire composition range at 298.15 K. Such  $H_{ijk}^E$  data may thus be of importance to meet the academic and industrial development demands of the society.

## Experimental

The ILs, CPO and CHO of highest purity (commercially available) were used in the present investigation. ILs studied in this paper were 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [Bmmim][BF<sub>4</sub>]; (mass fraction, *w*: 0.990), 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF<sub>4</sub>]; (*w*: 0.985) and 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF<sub>4</sub>]; (*w*: 0.990) obtained from Sigma-Aldrich. ILs were purified by vacuum treatment at residual pressure  $5 \times 10^{-2}$  Pa and at 338 K to eliminate the water and other volatile compound traces. The CPO (*w*: 0.990) and CHO (*w*: 0.990) were purified by standard means [29], and their final purity was checked by gas chromatography. The *w* of water in ILs and organic solvents was tested regularly by Karl Fischer titration method [30] and was observed to have maximum value of 0.0003. The purity, supplier, CAS number and analysis methods of the studied chemicals are reported in Table 1. The densities,  $\rho$ , and speeds of sound, *u*, values of the present ILs and cycloalkanones were measured, at 298.15 K and atmospheric pressure using a density and sound analyzer (Anton Paar DSA 5000) with an estimated accuracy

of  $\pm 1.2 \text{ kg m}^{-3}$  and  $\pm 0.5 \text{ m s}^{-1}$ , respectively, in the manner as described elsewhere [31, 32]. The working frequency of the instrument was 3 MHz. Such  $\rho$  and *u* values are reported and compared with their literature values [25, 26, 33–44] in Table 2.

The  $H_{ijk}^E$  data of the mixtures were measured by means of high-sensitivity micro-differential scanning calorimeter Micro DSC (Model- $\mu$ DSC 7 Evo), supplied M/S SETARAM, France, in the manner as described elsewhere [45]. The calorimeter uses a double-stage temperature control with Peltier coolers, and the minimum and maximum temperatures that can be reached are about (228.15–393.15) K, respectively. The temperature of the calorimeter was maintained at 298.15 K with the uncertainty of  $\pm 0.02$  K. A constant sweeping of nitrogen gas for about four hours (0.3–0.4) MPa pressure was supplied to avoid steam condensation in the calorimeter walls. After this period, 0.08 MPa pressure of nitrogen gas was maintained. The calibration of calorimeter was done by Joule effect method. The calibration was checked by measuring heat of fusion of naphthalene, which was found to be  $148.41 \text{ J g}^{-1}$  which in turn was comparable to literature value of  $148.7 \text{ J g}^{-1}$  [46]. The  $H_{ijk}^E$  values for (*i* + *j* + *k*) mixtures were measured by taking binary mixture of known composition (by mass) in the lower chamber of mixing batch cell and pure component (*k*) (by mass) in the upper chamber of mixing batch cell. The liquid in the upper vessel of mixing batch cell was taken with the help of micropipette (supplied by M/S SETARAM, capacity 10–50  $\mu$ l). The composition of liquid mixtures was prepared by mass using a digital electronic balance (Mettler AX-205) with an uncertainty of  $\pm 1 \times 10^{-5}$  g. The uncertainty in the estimation of mole fraction is  $\pm 1 \times 10^{-3}$ . The stability in the calorimeter signal was indicated by consistent heat flow and temperature line on the experimental setup screen. The temperature and isothermal levels were maintained by software provide by M/S SETARAM. After attaining the stability, the knob of the upper chamber of the mixing batch cell was pressed to inject component (*k*) to the lower chamber possessing (*i* + *j*) mixture. After isothermal level time, the data were automatically transferred to the experimental result tab and a graph was obtained between heat flow versus time. The area of the peak provided the amount of heat involved,  $Q_{ijk}$ , during the mixing process. The  $Q_{ijk}$  values were then used to determine  $H_{ijk}^E$  using

$$H_{ijk}^E = \frac{(Q_{ijk} + Q_{ij})}{(n_i + n_j + n_k)} \quad (1)$$

where  $Q_{ij}$  is the amount of heat evolved in the binary (*i* + *j*) mixtures of known composition and is calculated using  $H_{ij}^E$  values of (*i* + *j*) mixtures by using

**Table 1** Details of chemical source, their CAS number, purification method, final purities and analysis method

Chemical name	CAS number	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method	w of water <sup>b</sup>
[Bmmim][BF <sub>4</sub> ]	402846-78-0	Sigma-Aldrich	0.990	Drying	–		0.0002
[Bmim][BF <sub>4</sub> ]	174501-65-6	Sigma-Aldrich	0.985	Drying	–		0.0002
[Emim][BF <sub>4</sub> ]	143314-16-3	Sigma-Aldrich	0.990	Drying	–		0.0002
CPO	120-92-3	Sigma-Aldrich	0.990	Fractional distillation	0.995	GC <sup>a</sup>	0.0003
CHO	108-94-1	Sigma-Aldrich	0.990	Fractional distillation	0.993	GC <sup>a</sup>	0.0003

<sup>a</sup>Gas chromatography<sup>b</sup>Karl Fisher titration method was used to determine mass fraction of water**Table 2** Comparison of experimental densities,  $\rho$ , and speeds of sound,  $u$ , values of pure components with literature values at 298.15 K and atmospheric pressure ( $p = 0.1$  MPa)

Components	$\rho/\text{kg m}^{-3}$		$u/\text{m s}^{-1}$	
	Expt.	Lit.	Expt.	Lit.
[Bmmim][BF <sub>4</sub> ]	1191.80	1193.19 <sup>25</sup> 1191.2 <sup>33</sup> 1193.338 <sup>34</sup>	1645.7	1641.44 <sup>34</sup>
[Bmim][BF <sub>4</sub> ]	1198.93	1198.78 <sup>26</sup> 1199.387 <sup>35</sup>	1565.5	1565.09 <sup>26</sup> 1565.1 <sup>35</sup>
[Emim][BF <sub>4</sub> ]	1279.91	1280 <sup>36</sup> 1280.07 <sup>37</sup>	1619.2	1622.89 <sup>38</sup> 1629 <sup>39</sup>
CPO	944.53	944.52 <sup>40</sup> 944.35 <sup>41</sup> 945.3 <sup>42</sup>	1393.6	1393.2 <sup>40</sup> 1394.1 <sup>43</sup>
CHO	942.92	942.90 <sup>40</sup> 942.76 <sup>43</sup>	1414.5	1414.8 <sup>40</sup> 1408.0 <sup>44</sup>

Standard uncertainties,  $u$ , are  $u$  (T) (DSA) =  $\pm 0.01$  K;  $u$  ( $\rho$ ) =  $\pm 1.2$  kg m<sup>-3</sup>;  $u$  ( $u$ ) =  $\pm 0.5$  m s<sup>-1</sup>;  $u$  ( $x_i$ ) =  $\pm 1 \times 10^{-3}$ ;  $u$  ( $P$ ) =  $\pm 0.01$  MPa

$$Q_{ij} = H_{ij}^E(n_i + n_j) \quad (2)$$

where  $n_i$ ,  $n_j$  and  $n_k$  are number of moles of components in ternary mixtures. The  $H_{ij}^E$  values of binary ( $i + j$ ), ( $j + k$ ), ( $i + k$ ) mixtures constituting ternary mixtures were taken from the literature [27, 28, 40, 47]. The uncertainty in the determination of  $H_{ijk}^E$  values is  $\pm 1\%$ .

## Results

Table 3 presents the measured excess molar enthalpies,  $H_{ijk}^E$  values for ternary [Bmmim][BF<sub>4</sub>] ( $i$ ) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] ( $j$ ) + CPO or CHO ( $k$ ) mixtures over the entire mole fraction of ( $i$ ) and ( $j$ ) components at 298.15 K. The experimental  $H_{ijk}^E$  values for each mixture were

correlated by means of Redlich–Kister equation [48] in the form:

$$H_{ijk}^E = x_i x_j \left[ \sum_{n=0}^2 a_{ij}(n) (x_i - x_j)^n \right] + x_j x_k \left[ \sum_{n=0}^2 a_{jk}(n) (x_j - x_k)^n \right] + x_i x_k \left[ \sum_{n=0}^2 a_{ik}(n) (x_i - x_k)^n \right] + x_i x_j x_k \left[ \sum_{n=0}^2 a_{ijk}(n) (x_j - x_k)^n x_i^n \right] \quad (3)$$

where,  $x_i$ ,  $x_j$  and  $x_k$  are the mole fractions of ( $i$ ), ( $j$ ) and ( $k$ ) components. The Redlich–Kister parameters,  $a_{ij}(n)$ ,  $a_{jk}(n)$ ,  $a_{ik}(n)$ , ( $n = 0-2$ ) of binary mixtures ( $i + j$ ), ( $j + k$ ), ( $i + k$ ) of ( $i + j + k$ ) ternary mixture, were taken from the literature [27, 28, 40, 47] and are also reported in Table 4. The  $H^E$  data for ( $i + j$ ), ( $j + k$ ), ( $i + k$ ) of ( $i + j + k$ ) ternary mixture have been measured in the same laboratory by using same chemicals of comparable purity. The  $a_{ijk}(n)$  ( $n = 0-2$ ) are coefficients of ( $i + j + k$ ) mixture and are obtained by fitting the measured  $H_{ijk}^E$  data to Eq. (3) by least-squares methods. These coefficients along with the standard deviations,  $\sigma(H_{ijk}^E)$ , are presented in Table 5. The surfaces generated by  $H_{ijk}^E$  values for the studied ternary mixtures are shown in Figs. 1–4. In Fig. 1, the  $H_{ijk}^E$  values (corresponding to  $i-j$  axis) were obtained by keeping  $x_k$  constant and varying the values of  $x_i$  and  $x_j$  (shown as red line);  $H_{ijk}^E$  values (corresponding to  $j-k$  axis) were obtained by keeping  $x_i$  constant and varying the values  $x_j$  and  $x_k$  (shown as green line).

**Table 3** Comparison of experimental  $H_{ijk}^E$  data of the various ( $i + j + k$ ) mixtures at atmospheric pressure ( $p = 0.1$  MPa) with the values evaluated from graph theory at 298.15 K

$x_i$	$x_j$	$H_{ijk}^E / \text{J mol}^{-1}$	
		Expt.	Graph
[Bmmim][BF <sub>4</sub> ] ( $i$ ) + [Bmim][BF <sub>4</sub> ] ( $j$ ) + CPO ( $k$ )			
0.1288	0.7509	068.2	068.2
0.1402	0.7372	090.3	092.1
0.1601	0.7199	131.3	142.2
0.1825	0.7024	187.7	196.4
0.1978	0.6991	236.9	248.6
0.2145	0.6735	247.9	255.6
0.2215	0.6612	249.7	254.7
0.2389	0.6351	255.9	260.1
0.2523	0.6123	248.0	257.7
0.2613	0.5982	257.6	257.6
0.2843	0.5632	280.4	256.0
0.3459	0.4751	250.6	237.6
0.3628	0.4524	255.6	228.6
0.3710	0.4421	253.2	224.3
0.3931	0.4156	230.8	211.4
0.4048	0.4039	218.6	206.1
0.4242	0.3812	195.9	190.6
0.4463	0.3604	176.5	176.5
0.4538	0.3562	175.2	175.0
0.4671	0.3412	153.4	161.1
0.4854	0.3251	139.1	146.9
0.5142	0.3021	115.4	125.2
0.5208	0.2915	102.4	111.8
0.5342	0.2856	099.5	107.7
0.5566	0.2696	086.8	090.7
0.5707	0.2576	071.2	076.5
0.5863	0.2475	065.5	065.5
0.6055	0.2336	054.9	049.4
0.6245	0.2209	037.7	035.0
0.6546	0.2005	010.8	012.0
0.6887	0.1812	008.2	008.3
0.7089	0.1665	005.6	005.5
0.7153	0.1422	002.2	002.1
[Bmmim][BF <sub>4</sub> ] ( $i$ ) + [Bmim][BF <sub>4</sub> ] ( $j$ ) + CHO ( $k$ )			
0.1381	0.7165	075.9	076.0
0.1522	0.6917	098.4	078.1
0.1751	0.6691	150.7	160.2
0.1943	0.6433	184.1	185.4
0.2294	0.6273	356.7	383.5
0.2452	0.5956	303.1	326.0
0.2642	0.5783	343.4	369.8
0.2814	0.5549	357.7	357.7
0.3078	0.5375	417.4	440.5
0.3245	0.5124	399.7	398.4

**Table 3** (continued)

$x_i$	$x_j$	$H_{ijk}^E / \text{J mol}^{-1}$	
		Expt.	Graph
0.3456	0.4906	407.5	400.1
0.3625	0.4776	433.0	425.3
0.3822	0.4618	446.0	445.9
0.3947	0.4427	401.0	393.2
0.4002	0.4244	322.6	302.3
0.4234	0.4088	351.3	329.9
0.4429	0.3961	352.5	352.5
0.4592	0.3742	292.9	286.2
0.4779	0.3578	274.0	268.6
0.4988	0.3334	206.5	198.3
0.5163	0.3271	231.8	242.8
0.5322	0.3036	145.6	143.2
0.5514	0.2872	115.6	112.0
0.5708	0.2660	039.0	040.1
0.5973	0.2583	100.3	110.1
0.6084	0.2475	075.7	075.7
0.6215	0.2222	– 064.0	– 071.9
0.6452	0.2083	– 068.4	– 075.0
0.6605	0.1981	– 090.3	– 087.9
0.6819	0.1867	– 086.3	– 081.0
0.7081	0.1633	– 079.3	– 077.2
0.7221	0.1464	– 070.1	– 068.4
[Bmmim][BF <sub>4</sub> ] ( $i$ ) + [Emim][BF <sub>4</sub> ] ( $j$ ) + CPO ( $k$ )			
0.1661	0.7230	041.6	041.6
0.1882	0.6971	155.0	157.0
0.1995	0.6838	210.9	209.2
0.2111	0.6703	246.1	260.3
0.2373	0.6404	374.7	367.1
0.2592	0.6131	407.5	414.9
0.2765	0.5936	444.9	465.8
0.2986	0.5703	515.8	534.9
0.3201	0.5466	554.0	577.9
0.3367	0.5263	568.1	583.1
0.3579	0.5030	605.8	605.8
0.3768	0.4817	620.0	612.1
0.3980	0.4595	645.4	624.7
0.4203	0.4358	643.1	624.2
0.4435	0.4154	653.0	647.3
0.4555	0.4036	648.8	644.4
0.4924	0.3689	627.0	630.5
0.5071	0.3559	617.1	624.0
0.5214	0.3432	613.7	613.7
0.5458	0.3199	566.4	578.3
0.5741	0.2939	519.6	535.4
0.5967	0.2731	479.3	495.7
0.6255	0.2468	434.1	442.2
0.6605	0.2187	393.4	389.7

**Table 3** (continued)

$x_i$	$x_j$	$H_{ijk}^E / J \text{ mol}^{-1}$	
		Expt.	Graph
0.6869	0.1946	344.9	338.7
0.7082	0.1754	304.1	302.2
0.7296	0.1567	273.8	271.5
0.7525	0.1371	246.0	246.0
0.7609	0.1297	237.9	238.8
0.7835	0.1069	230.4	232.4
[Bmmim][BF <sub>4</sub> ] (i) + [Emim][BF <sub>4</sub> ] (j) + CHO (k)			
0.1069	0.7814	- 071.7	- 067.9
0.1235	0.7691	- 111.1	- 111.1
0.1419	0.7456	- 130.3	- 139.5
0.1553	0.7302	- 142.0	- 158.7
0.1788	0.7146	- 181.4	- 194.5
0.1913	0.7087	- 203.4	- 209.9
0.2029	0.6954	- 212.2	- 215.7
0.2147	0.6819	- 215.8	- 219.6
0.2416	0.6518	- 219.3	- 222.0
0.2640	0.6245	- 208.3	- 217.1
0.3043	0.5812	- 194.8	- 194.8
0.3263	0.5572	- 177.7	- 175.8
0.3435	0.5368	- 155.1	- 159.4
0.3652	0.5132	- 130.2	- 134.5
0.3846	0.4916	- 105.6	- 110.5
0.4063	0.4691	- 074.8	- 079.7
0.4291	0.4449	- 043.1	- 046.4
0.4526	0.4240	- 003.8	- 003.8
0.4648	0.4119	016.7	016.7
0.4772	0.3996	037.5	037.5
0.5024	0.3763	080.2	083.5
0.5172	0.3630	102.7	111.4
0.5317	0.3500	128.5	138.3
0.5565	0.3262	169.7	177.7
0.5852	0.2996	209.4	221.2
0.6080	0.2783	240.1	249.7
0.6371	0.2514	277.8	278.2
0.6721	0.2226	308.3	315.4
0.6988	0.1980	315.3	315.3
0.7202	0.1784	318.4	304.4

Standard uncertainties,  $u$ , are  $u(T)$  (DSC) =  $\pm 0.02$  K;  $u(x_i)$  =  $\pm 1 \times 10^{-3}$ ;  $u(H_{ijk}^E)$  =  $\pm 1\%$ ;  $u(P)$  =  $\pm 0.01$  MPa

## Discussion

We are unaware of any published  $H_{ijk}^E$  data of investigated mixtures with which to compare our results. The  $H_{ijk}^E$  values for [Bmmim][BF<sub>4</sub>] (i) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (j) + CPO (k) mixtures are endothermic over whole range of composition of  $x_i$  and  $x_j$ . However, sign and

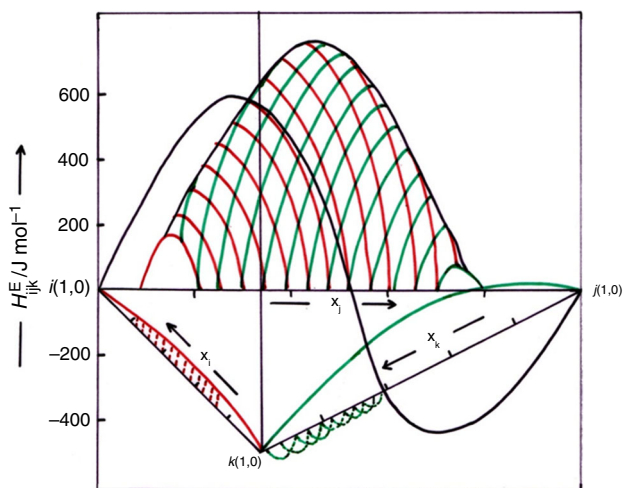
**Table 4** Binary adjustable parameters,  $a_{ij}(n)$ ,  $a_{jk}(n)$ ,  $a_{ik}(n)$  ( $n = 0-2$ ) along with standard deviations,  $\sigma(H^E)$  for the constituent binary mixtures of studied ternary mixtures at 298.15 K

$a_0/J \text{ mol}^{-1}$	$a_1/J \text{ mol}^{-1}$	$a_2/J \text{ mol}^{-1}$	$\sigma(H^E)/J \text{ mol}^{-1}$
[Bmmim][BF <sub>4</sub> ] (i) + [Bmim][BF <sub>4</sub> ] (j)			
206	- 38.5	- 89.9	0.52
[Bmmim][BF <sub>4</sub> ] (i) + [Emim][BF <sub>4</sub> ] (j)			
336	4428	66.0	2.05
[Bmmim][BF <sub>4</sub> ] (i) + CPO (j)			
184	- 3.10	- 80.0	0.27
[Bmmim][BF <sub>4</sub> ] (i) + CHO (j)			
297	- 53.1	- 37.5	0.53
[Bmim][BF <sub>4</sub> ] (i) + CPO (j)			
- 188	- 21.2	45.6	0.31
[Bmim][BF <sub>4</sub> ] (i) + CHO (j)			
83.3	- 282	- 130	0.20
[Emim][BF <sub>4</sub> ] (i) + CPO (j)			
1997	- 121	12.3	1.40
[Emim][BF <sub>4</sub> ] (i) + CHO (j)			
2561	5.60	- 244	4.45

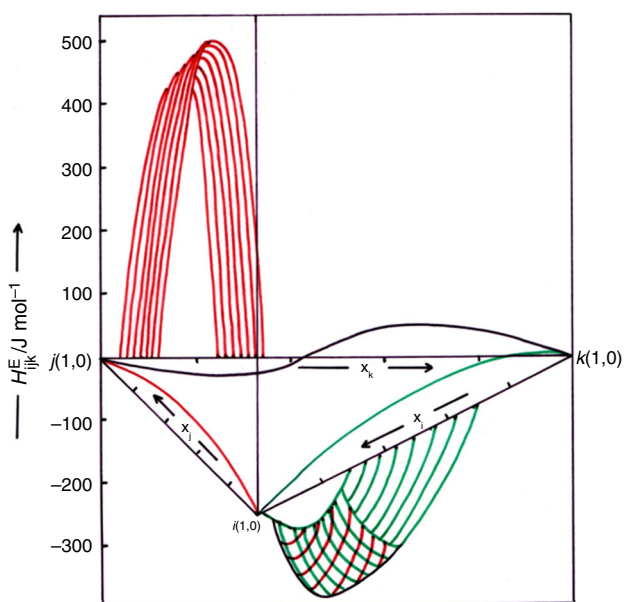
**Table 5** Ternary adjustable parameters,  $a_{ijk}(n)$  ( $n = 0-2$ ) parameters together with the standard deviations,  $\sigma(H_{ijk}^E)$  for the various ternary mixtures at 298.15 K

$a_{ijk}(0)/J \text{ mol}^{-1}$	$a_{ijk}(1)/J \text{ mol}^{-1}$	$a_{ijk}(2)/J \text{ mol}^{-1}$	$\sigma(H_{ijk}^E)/J \text{ mol}^{-1}$
[Bmmim][BF <sub>4</sub> ] (i) + [Bmim][BF <sub>4</sub> ] (j) + CPO (k)			
- 3482.0	87,312.3	266,174.1	1.6
[Bmmim][BF <sub>4</sub> ] (i) + [Bmim][BF <sub>4</sub> ] (j) + CHO (k)			
- 8086.6	93,038.4	830,351.2	2.4
[Bmmim][BF <sub>4</sub> ] (i) + [Emim][BF <sub>4</sub> ] (j) + CPO (k)			
- 12,983.2	132,015.0	955,195.3	3.6
[Bmmim][BF <sub>4</sub> ] (i) + [Emim][BF <sub>4</sub> ] (j) + CHO (k)			
- 8142.7	31,402.3	- 340,718.0	1.8

magnitude of  $H_{ijk}^E$  values for [Bmmim][BF<sub>4</sub>] (i) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (j) + CHO (k) mixtures are dictated by relative proportion of the components in the mixture. The  $H_{ijk}^E$  results from the disruption of interactions among the like molecules and the introduction of new interactions between the unlike molecules. The endothermic behavior of [Bmmim][BF<sub>4</sub>] (i) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (j) + CPO (k) mixtures reveals that the contribution to  $H_{ijk}^E$  due to disruption of cohesion forces in ILs and dipole-dipole interaction in CPO far outweighs the contribution due to interaction of CPO with [Bmmim][BF<sub>4</sub>]:[Bmim][BF<sub>4</sub>] and

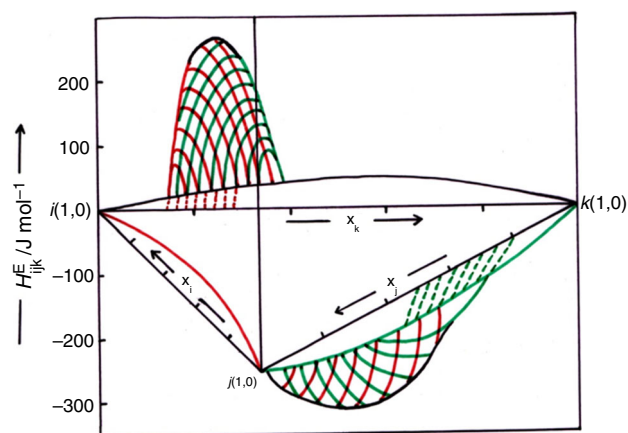


**Fig. 3** Excess molar enthalpies,  $H_{ijk}^E$  for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (*i*) + 1-ethyl-3-methylimidazolium tetrafluoroborate (*j*) + cyclopentanone (*k*) mixture at 298.15 K; experimental data in front of the plane (solid line); experimental data behind the plane (dashed line)

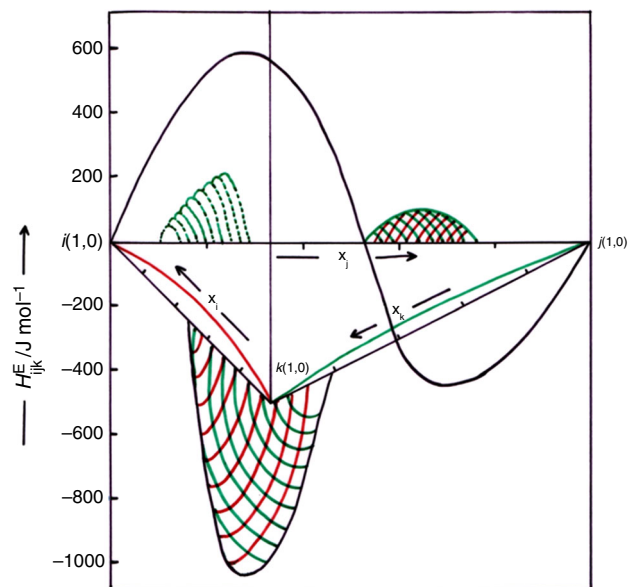


**Fig. 2** Excess molar enthalpies,  $H_{ijk}^E$  for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (*i*) + 1-butyl-3-methylimidazolium tetrafluoroborate (*j*) + cyclohexanone (*k*) mixture at 298.15 K; experimental data in front of the plane (solid line); experimental data behind the plane (dashed line)

[Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] molecular entities. The  $H_{ijk}^E$  values for [Bmmim][BF<sub>4</sub>] (*i*) + [Emim][BF<sub>4</sub>] (*j*) + CHO (*k*) are lesser than [Bmmim][BF<sub>4</sub>] (*i*) + [Emim][BF<sub>4</sub>] (*j*) + CPO (*k*) mixture which in turn indicate strong interactions among the CHO and [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] in comparison with CPO and [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] molecular entity. This may be



**Fig. 1** Excess molar enthalpies,  $H_{ijk}^E$  for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (*i*) + 1-butyl-3-methylimidazolium tetrafluoroborate (*j*) + cyclopentanone (*k*) mixture at 298.15 K; experimental data in front of the plane (solid line); experimental data behind the plane (dashed line)



**Fig. 4** Excess molar enthalpies,  $H_{ijk}^E$  for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (*i*) + 1-ethyl-3-methylimidazolium tetrafluoroborate (*j*) + cyclohexanone (*k*) mixture at 298.15 K; experimental data in front of the plane (solid line); experimental data behind the plane (dashed line)

due to behavior of CHO (being more basic in nature than CPO and also possess chair form with almost no strain) that results in strong interactions/effectively packing of CHO in the [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] framework as compared to CPO. Further, the higher  $H_{ijk}^E$  values for [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] (*j*) + CPO or CHO (*k*) than [Bmmim][BF<sub>4</sub>] (*i*) + [Emim][BF<sub>4</sub>] (*j*) + CPO or CHO (*k*) mixtures suggest least interactions between CPO or CHO with [Bmmim][BF<sub>4</sub>]:[Bmim][BF<sub>4</sub>] in comparison

with [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] molecular entity. This trend may be explained on the basis of steric effect where the presence of bulky butyl group in side chain of [Bmim][BF<sub>4</sub>] obstructs the approach of CPO or CHO toward [Bmmim][BF<sub>4</sub>]:[Bmim][BF<sub>4</sub>] in comparison with [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] molecular entity.

## Graph theory

### Conceptual aspects of graph theory

Molecular topology has been widely used in a variety of areas such as in the discovery and design of new drugs, molecule design, prediction of physicochemical parameters, pharmacological properties, mathematical models for the selection and design of new active compounds [49]. Molecular topology of a molecule depends upon the manner in which the components of a particular species are being associated with each other and thus correlates between a given physical, chemical, or biological property with the corresponding molecular characterization provided by some numerical invariants known as topological indices. The purpose of these indices is to codify the physicochemical properties of a molecule in a purely numerical fashion. A variety of topological indices [50–53] have been proposed, and a number of investigations have been made to extend and apply them in structure activity studies for encoding the structural information. The connectivity parameter of third degree of a molecule,  ${}^3\xi$  (which in turn depends upon its topology), has been successfully utilized to build relation between the thermodynamic properties ( $V^E$ ,  $\kappa_S^E$ ,  $H^E$ ,  $C_p^E$ ) of binary/ternary liquid mixtures and the corresponding molecular characterization provided by the constituents of mixtures. In the present study, connectivity parameters of third degree of the constituent molecules of mixtures have been successfully utilized to predict  $H_{ijk}^E$  data of ternary mixtures.

### Graph theory and results

The  $H^E$  data of liquid mixtures can be tested in terms of graph theory if the states of components in pure and mixed states are known. In our earlier studies [27, 28, 40, 47], thermodynamic and topological analyses of excess properties ( $V^E$ ,  $\kappa_S^E$ ,  $H^E$  and  $C_p^E$ ) of [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (*j*); [Bmmim][BF<sub>4</sub>] or [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (*i*) + CPO or CHO (*j*) binary mixtures have suggested that ILs: [Bmmim][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>] and [Emim][BF<sub>4</sub>], are characterized by cohesion forces between (a) hydrogen atom of C–H (edge) of imidazolium ring and two fluorine atoms of BF<sub>4</sub>;

(b) proton of CH<sub>3</sub> group of imidazolium ring and two fluorine atoms of BF<sub>4</sub> and exists as monomer; (c) CPO or CHO is characterized by dipole–dipole interactions and exists as associated molecular entities.

Quantum mechanical and infrared (IR) spectral studies also support this view point [27, 28, 40, 47, 54–61].

Scheme 1 represents the connectivity parameters of third degree of the components [27, 28, 40, 47] and various inter-nuclear distances among interacting atoms (predicted by quantum mechanical calculations using Gaussian program package 09) in [Bmmim][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>], [Emim][BF<sub>4</sub>], CPO and CHO.

The energetics of ternary mixtures can be studied if it be assumed that the addition of component (*k*) to (*i* + *j*) mixture leads to the formation of (*i* + *j* + *k*) mixture that may involve the processes: (I) formation of unlike (a) *i* – *j*, (b) *j* – *k<sub>n</sub>* (*n* = 2), (c) *i* – *k<sub>n</sub>* contacts and (II) unlike contact formation then cause the rupture of (a–b) cohesion forces in pure ILs, [Bmmim][BF<sub>4</sub>] or [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>], and (c) dipole–dipole interactions in CPO or CHO to yield their respective monomers; (III) specific interactions between *i*, *j* and *k* molecules lead to the formation of (a) *i*:*j*; (b) *j*:*k*; and (c) *i*:*k* molecular complexes.

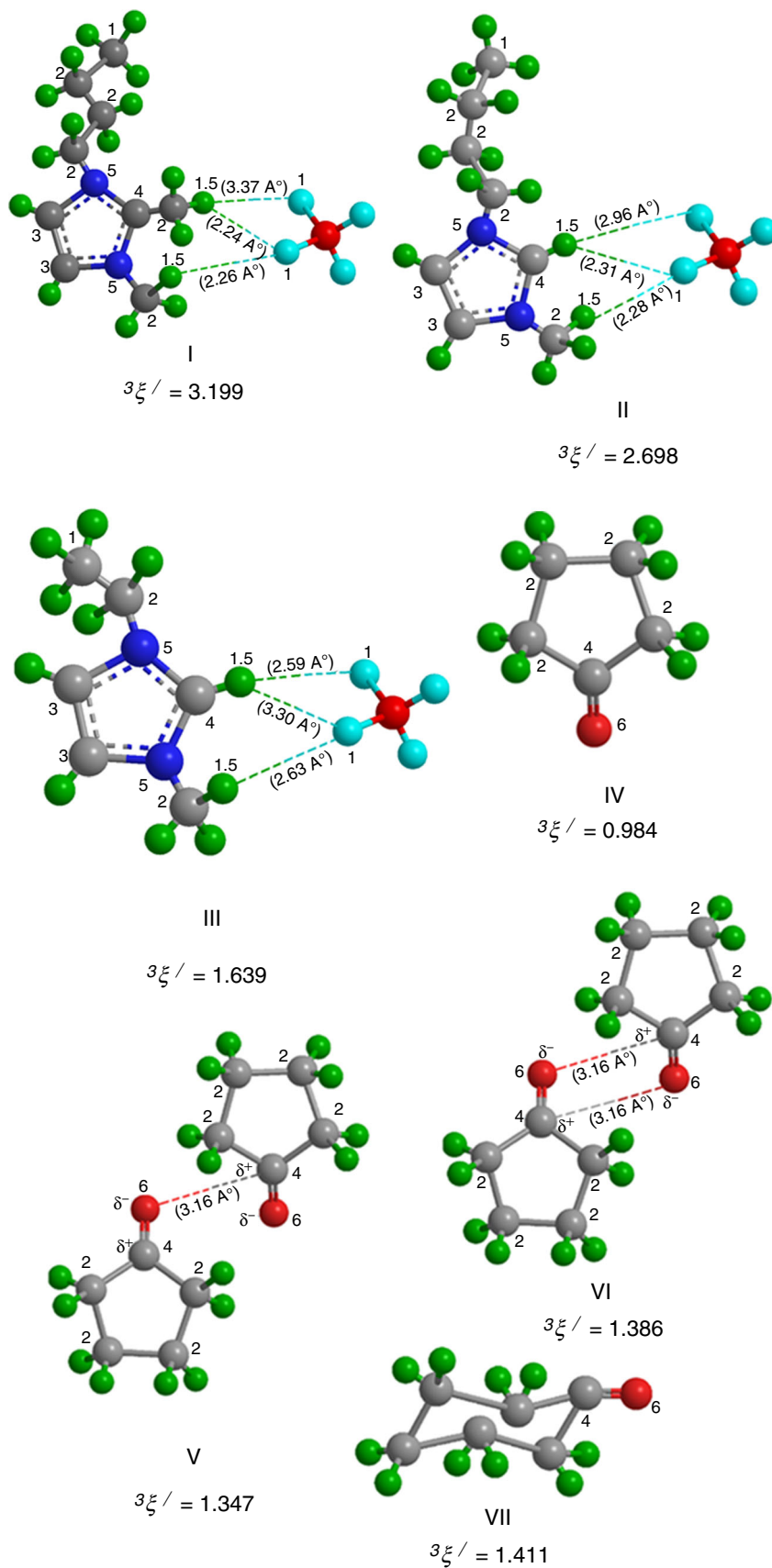
If  $\chi_{ij}$ ,  $\chi_{jk}$ ;  $\chi_{ii}$ ,  $\chi_{ij}\chi_{kk}\chi_{ik}$ ; and  $\chi'_{ij}$ ,  $\chi''_{jk}$ ,  $\chi'''_{ik}$  are molar interaction parameters for (I) establishment of unlike (a) *i* – *j*, (b) *j* – *k<sub>n</sub>* (*n* = 2), (c) *i* – *k<sub>n</sub>* contacts; (II) rupture of cohesion forces (a–b) in ILs and (c) dipole–dipole interactions in CPO and CHO; and (III) formation of *i*:*j*, *j*:*k*, *i*:*k* molecular complexes, respectively.

Then change in molar enthalpies,  $\Delta H$ , due to processes (I) (a)–(c); (II) (a)–(c); and (III) (a)–(c) are then expressed by [62–64]:

$$\Delta H_I = \left[ \frac{x_i x_j v_j}{\sum_{i=i}^j x_i v_i} \right] [\chi_{ij}] + \left[ \frac{x_j x_k v_k}{\sum_{j=j}^k x_j v_j} \right] [\chi_{jk}] + \left[ \frac{x_k x_i v_i}{\sum_{k=k}^i x_k v_k} \right] [\chi_{ik}] \quad (4)$$

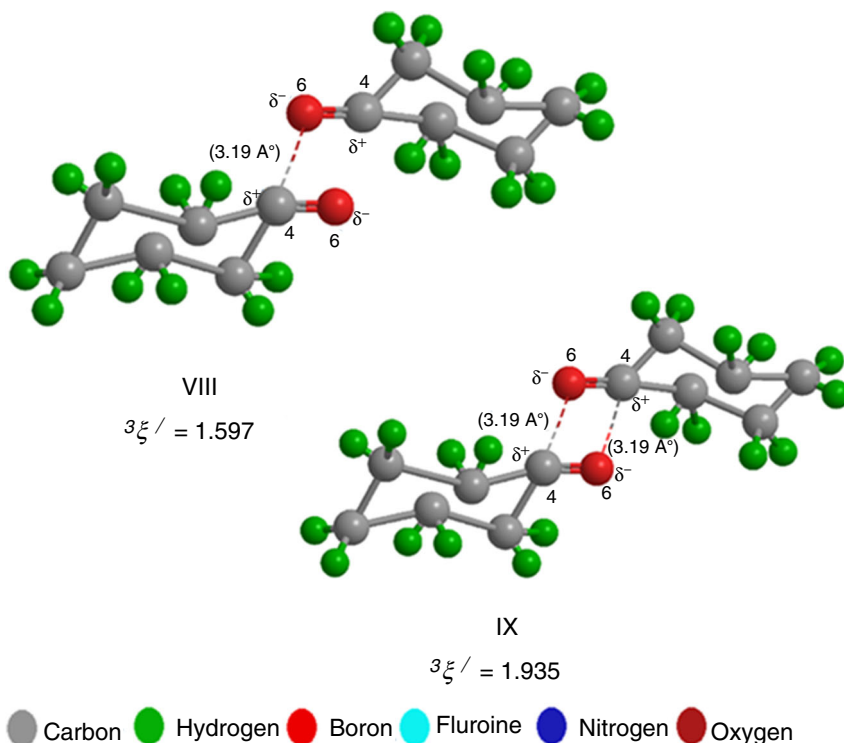
$$\Delta H_{II} = \left[ \frac{x_i^2 x_j v_j}{\sum_{i=i}^j x_i v_i} \right] [\chi_{ii}] + \left[ \frac{x_j^2 x_k v_k}{\sum_{j=j}^k x_j v_j} \right] [\chi_{jj}] + \left[ \frac{x_k^2 x_i v_i}{\sum_{k=k}^i x_k v_k} \right] [\chi_{kk}] \quad (5)$$

**Scheme 1** Connectivity parameters,  ${}^3\xi/$ , of the third degree for various molecular entities





Scheme 1 continued



$$\Delta H_{\text{III}} = \left[ \frac{x_i x_j^2 v_j}{\sum_{i=i}^j x_i v_i} \right] [\chi_{ij}^{\prime}] + \left[ \frac{x_j x_k^2 v_k}{\sum_{j=j}^k x_j v_j} \right] [\chi_{jk}^{\prime\prime}] + \left[ \frac{x_k x_i^2 v_i}{\sum_{k=k}^i x_k v_k} \right] [\chi_{ik}^{\prime\prime\prime}] \quad (6)$$

where  $v_i$ ,  $v_j$  and  $v_k$  are the molar volumes of components (i), (j) and (k), respectively.

The total change in  $H_{ijk}^E$  values due to processes: (I) (a)–(c); (II) (a)–(c); and (III) (a)–(c) is presented by:

$$H_{ijk}^E = \sum_{i=1}^{\text{III}} (\Delta H_i) = \left[ \frac{x_i x_j v_j}{\sum_{i=i}^j x_i v_i} \right] [\chi_{ij} + x_i \chi_{ii} + x_j \chi_{ij}^{\prime}] + \left[ \frac{x_j x_k v_k}{\sum_{j=j}^k x_j v_j} \right] [\chi_{jk} + x_j \chi_{jj} + x_k \chi_{jk}^{\prime\prime}] + \left[ \frac{x_k x_i v_i}{\sum_{k=k}^i x_k v_k} \right] [\chi_{ik} + x_k \chi_{kk} + x_i \chi_{ik}^{\prime\prime\prime}] \quad (7)$$

It has further been shown [65] that  $1/3^\xi$  of a molecule represents a measure of the probability that its surface area interacts effectively with the corresponding surface area of other molecule and within the same isomeric species; molar volume of a molecule varies inversely as its  $3^\xi$ . Consequently,  $v_j/v_i = (3^\xi_i/3^\xi_j)$  [66] where  $(3^\xi_i)$ , ( $i = i$  or  $j$  or  $k$ ) are the connectivity parameter of third degree of components (i), (j) and (k), respectively, and are defined by

$$3^\xi = \sum_{m < n < o < p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \quad (8)$$

where  $\delta_m^v$  values define [67] the valency of  $m$ th vertex used in the formation of the bond and has been calculated by employing relation  $\delta^v = Z_m - h$ . ( $Z_m$  is related to maximum valency of atom and  $h$  is the number of hydrogen atoms attached to it.)

Equation 7 is, therefore, reduced to:

$$H_{ijk}^E = \sum_{i=1}^{\text{III}} (\Delta H_i) = \left[ \frac{x_i x_j (3^\xi_i/3^\xi_j)}{x_i + x_j (3^\xi_i/3^\xi_j)} \right] [\chi_{ij} + x_i \chi_{ii} + x_j \chi_{ij}^{\prime}] + \left[ \frac{x_j x_k (3^\xi_j/3^\xi_k)}{x_j + x_k (3^\xi_j/3^\xi_k)} \right] [\chi_{jk} + x_j \chi_{jj} + x_k \chi_{jk}^{\prime\prime}] + \left[ \frac{x_k x_i (3^\xi_k/3^\xi_i)}{x_k + x_i (3^\xi_k/3^\xi_i)} \right] [\chi_{ik} + x_k \chi_{kk} + x_i \chi_{ik}^{\prime\prime\prime}] \quad (9)$$

In the present mixtures, it was assumed that (1) molar interaction parameters for the formation of unlike contacts

**Table 6** Connectivity parameters of third degree of a molecule,  ${}^3\xi_i$  ( $i = i$  or  $j$  or  $k$ ) along with interaction energy parameters,  $\chi_{ij}^*$ ,  $\chi_{jk}^*$ ,  $\chi_{ik}^*$ ,  $\chi^*$  of Eq. (10) at 298.15 K

Connectivity parameters			Interaction energy parameters/J mol <sup>-1</sup>				$\sigma(H_{ijk}^E)$ J mol <sup>-1</sup>
${}^3\xi_i$	${}^3\xi_j$	${}^3\xi_k$	$\chi_{ij}^*$	$\chi_{jk}^*$	$\chi_{ik}^*$	$\chi^*$	
[Bmmim][BF <sub>4</sub> ] ( <i>i</i> ) + [Bmim][BF <sub>4</sub> ] ( <i>j</i> ) + CPO ( <i>k</i> )							
3.403	2.396	1.287	2255.7	161.2	- 745.9	- 2610.3	11.8
[Bmmim][BF <sub>4</sub> ] ( <i>i</i> ) + [Bmim][BF <sub>4</sub> ] ( <i>j</i> ) + CHO ( <i>k</i> )							
3.403	2.396	2.105	4524.4	- 3412.4	- 3804.6	- 908.7	12.7
[Bmmim][BF <sub>4</sub> ] ( <i>i</i> ) + [Emim][BF <sub>4</sub> ] ( <i>j</i> ) + CPO ( <i>k</i> )							
3.403	1.639	1.287	6402.5	- 7080.0	4609.1	- 7797.1	11.4
[Bmmim][BF <sub>4</sub> ] ( <i>i</i> ) + [Emim][BF <sub>4</sub> ] ( <i>j</i> ) + CHO ( <i>k</i> )							
3.403	1.639	2.105	- 1530.1	- 2017.1	- 3960.4	7358.3	7.4

$i - j$ ;  $j - k$ ;  $i - k$  are nearly equal to molar interaction parameters for the establishment of  $i:j$ ,  $j:k$ ,  $i:k$  molecular complexes, and (2) molar interaction parameter for the dissociation of cohesion forces in ILs and dipole–dipole interactions in cycloalkanone is nearly equal, i.e.,  $\chi_{ij} \cong \chi_{ij}' = \chi_{ij}^*$ ;  $\chi_{jk} \cong \chi_{jk}' = \chi_{jk}^*$ ;  $\chi_{ik} \cong \chi_{ik}' = \chi_{ik}^*$ ;  $\chi_{ii} \cong \chi_{jj} \cong \chi_{kk} = \chi^*$ ; Eq. (9) is then expressed as:

$$H_{ijk}^E = \left[ \frac{x_i x_j ({}^3\xi_i / {}^3\xi_j)}{x_i + x_j ({}^3\xi_i / {}^3\xi_j)} \right] [(1 + x_j)\chi_{ij}^* + x_i \chi^*] + \left[ \frac{x_j x_k ({}^3\xi_j / {}^3\xi_k)}{x_j + x_k ({}^3\xi_j / {}^3\xi_k)} \right] [(1 + x_k)\chi_{jk}^* + x_j \chi^*] + \left[ \frac{x_k x_i ({}^3\xi_k / {}^3\xi_i)}{x_k + x_i ({}^3\xi_k / {}^3\xi_i)} \right] [(1 + x_i)\chi_{ik}^* + x_k \chi^*] \quad (10)$$

The four unknown parameters:  $\chi_{ij}^*$ ,  $\chi_{jk}^*$ ,  $\chi_{ik}^*$  and  $\chi^*$ , in Eq. (10) are commuted using  $H_{ijk}^E$  data at four arbitrary compositions and then subsequently used to calculate  $H_{ijk}^E$  values at other mole fractions of  $x_i$  and  $x_j$ . Such  $H_{ijk}^E$  values for investigated mixtures are reported in Table 3 and also compared with the corresponding experimental values. The  $\chi_{ij}^*$ ,  $\chi_{jk}^*$ ,  $\chi_{ik}^*$  and  $\chi^*$  parameters are listed in Table 6 along with standard deviations,  $\sigma(H_{ijk}^E)$  between experimental and theoretical calculated values. A perusal of data in Table 3 indicates a good agreement between calculated (by graph theory) and experimental  $H_{ijk}^E$  data, which in turn support the various assumptions made regarding the various processes involved in the mixture formation and also in deriving Eq. (10).

## Conclusions

The present work reports excess molar enthalpies,  $H_{ijk}^E$  data for [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] or [Emim][BF<sub>4</sub>] (*j*) + CPO or CHO (*k*) mixtures over the entire mole

fraction of (*i*) and (*j*) components at 298.15 K. The analyses of  $H_{ijk}^E$  data of [Bmmim][BF<sub>4</sub>] (*i*) + [Emim][BF<sub>4</sub>] (*j*) + CHO (*k*) mixture suggest that CHO molecules have been effectively packed in the lattices of [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>] molecular entity in comparison with CPO molecules. However, reverse is the trend in case of [Bmmim][BF<sub>4</sub>] (*i*) + [Bmim][BF<sub>4</sub>] (*j*) + CHO (*k*) mixture. The  $H_{ijk}^E$  values of studied (*i* + *j* + *k*) mixtures also indicate least interactions between CPO and CHO with [Bmmim][BF<sub>4</sub>]:[Bmim][BF<sub>4</sub>] in comparison with [Bmmim][BF<sub>4</sub>]:[Emim][BF<sub>4</sub>]. The  $H_{ijk}^E$  data of the present mixtures have also been tested in terms of graph theory. It has been observed that  $H_{ijk}^E$  values computed by graph theory are in agreement with experimental values.

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