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# Thermodynamic investigations of excess heat capacities of ternary liquid mixtures containing [Bmmim][$BF_4$] + [Bmim][$BF_4$] or [Emim][$BF_4$] + cyclopentanone or cyclohexanone

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**Abstract** In this paper, molar heat capacities $(C_P)_{123}$ data of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [Bmmim][$BF_4$] (1) + 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][$BF_4$] or 1-ethyl-3-methylimidazolium tetrafluoroborate, [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures have been reported over the entire range of composition at (293.15, 298.15, 303.15, 308.15) K using micro-differential scanning calorimeter (Model—μDSC 7 Evo). The results have been utilized to calculate excess heat capacities $\left(C_P^E\right)_{123}$ values of the studied mixtures. The $\left(C_P^E\right)_{123}$ data have been fitted to Redlich–Kister equation to obtain ternary coefficients and standard deviations. The Moelwyn–Huggins concept of interaction between the surfaces of constituents of binary mixtures (Huggins in J Phys Chem 74:371–378, 1970) containing ionic liquid as one of the component has been extended to obtain expression (Graph theory) for $\left(C_P^E\right)_{123}$ of ternary mixtures. The comparison between experimental and estimated values (Graph theory) suggests that while 1-butyl-2,3-dimethylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate exists as monomer, cyclopentanone or cyclohexanone exists as mixture of open and cyclic dimer. The results further support the various processes involved in the formation of present mixtures. The $\left(C_P^E\right)_{123}$ values have also been tested in term of modified Flory's theory.

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**Keywords** 1-butyl-2,3-dimethylimidazolium tetrafluoroborate · Micro-DSC · Excess heat capacities · $\left(C_P^E\right)_{123}$, connectivity parameter of third degree · ${}^3\xi$, interaction energy parameter, $\chi$

## Introduction

Thermodynamic properties of liquid mixtures have great importance in theoretical and applied areas of research. The knowledge of these properties is frequently used in the design processes like flow, mass transfer or heat transfer calculations of many chemical and industrial processes [1–3]. Also these properties of liquid mixtures represent a useful complementary tool to extract the information about the structural features of the constituents of the mixture in pure as well as mixed state. The molar heat capacity, $C_P$, of a substance is a basic pure component property which plays a central role in all processes involving the uptake, release or transfer of heat energy and thus can be utilized for many engineering calculations [4–6]. Molar heat capacities, $C_P$, and excess heat capacities, $C_P^E$, of liquid mixtures are most needed properties in the design as well as optimization of the industrial processes such as food processing, estimation of heating or cooling requirements, heat storage capacity and also of equipment in the part where heat transfer is important [7–10].

In recent studies, excess heat capacities, $C_P^E$, of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate (2); 1-butyl-2,3-dimethylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + cyclopentanone or cyclohexanone (2) binary

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ionic liquid mixtures have been reported over entire composition range at (293.15, 298.15, 303.15 and 308.15) K. The topology of the constituent molecules (Graph theory) has been successfully utilized to compute excess heat capacities $C_P^E$ of the studied mixtures [11–14]. In the present paper, we extend our study to ternary mixtures and report excess heat capacities, $\left(C_P^E\right)_{123}$, of ternary 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate (2) + cyclopentanone or cyclohexanone (3) mixtures over the temperature range (293.15–308.15) K having interval of 5 K. The $\left(C_P^E\right)_{123}$ data of the said mixtures are not available in the literature. Further, it would be of interest to show how the Graph theory (which in turn deals with the topology of the constituent molecules) describes the $\left(C_P^E\right)_{123}$ values of present ternary mixtures. These considerations prompted use to measure molar heat capacities $(C_P)_{123}$ data of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate (2) + cyclopentanone or cyclohexanone (3) mixtures at (293.15, 298.15, 303.15 and 308.15) K.

## Experimental

### Materials

Ionic liquids (ILs) used in this work: 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [Bmmim][$BF_4$]; (mass fraction: ≥0.998), 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][$BF_4$]; (mass fraction: ≥0.993) and 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][$BF_4$]; (mass fraction: ≥0.990) obtained from Fluka were used for measurements without further purification. The water content in present ILs was estimated periodically by Karl Fischer Titration and was found to be less than (180–220) ppm [15]. Cyclopentanone (Fluka, mass fraction: ≥0.995) and cyclohexanone (Fluka, mass fraction: ≥0.990) were purified by standard methods [16]. The purification procedure and analysis methods of all chemicals used in this study along with their suppliers, CAS number and stated purities are given in Table 1.

The densities, $\rho$, and speeds of sound, $u$, values were measured to check the purity of the purified liquids at the studied temperatures using an vibrating tube densitometer (Anton Paar DSA 5000) with an estimated accuracy of ±0.5 kg $m^{-3}$ and 0.5 m $s^{-1}$, respectively, in the manner as described elsewhere [17, 18]. Such $\rho$ and $u$ values along with their literature values [14, 19–37] are reported in Table 2. It has been observed that measured $\rho$ and $u$ values are in agreement with the literature values.

### Apparatus and procedure

Molar heat capacities of pure liquids and the investigated ternary mixtures were measured by a high-sensitivity micro-differential scanning calorimeter Micro-DSC (Model—μDSC 7 Evo), from M/S SETARAM, France, in the manner as described elsewhere [38]. The calorimeter is based on the Tian–Calvet principle, which determines the change of heat flow from/to the liquid sample upon temperature scanning of 0.4 °C $min^{-1}$ and uses a double-stage temperature control with Peltier coolers that works between −45 and 120 °C. The calibration of calorimeter was done by Joule effect method and checked by measuring heat of fusion of naphthalene which was found to be 148.51 J $g^{-1}$ which in turn was comparable to literature value 148.7 J $g^{-1}$ [39]. The instrument is comprised of two differentially assembled reference and experimental batch cells lodged in a calorimetric block immersed in an inert atmosphere of nitrogen gas (constant sweeping of nitrogen gas at 0.8 bar pressure). Pure liquid or a mixture of known composition was taken in the experimental batch cell with the help of micropipette. Ternary mixtures were prepared by weighing the components using a digital electronic balance (Mettler AX-205) with an uncertainty of ±1 × $10^{-5}$ g for all measurements and kept in air-tight glass bottles to minimize the absorption of atmospheric moisture. The estimated uncertainty in the mole fraction was found to be ±1 × $10^{-4}$. The equipment was scanned for temperature cycle 15 °C (initial temperature) and 45 °C (final temperature) at the scanning (heating or cooling) rate 0.4 °C $min^{-1}$. The stability in the calorimetric signal was

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

| Chemical name | Source | CAS number | Purification method | Final purity (mass fraction) | Analysis method |
|---|---|---|---|---|---|
| 1-butyl-2,3-dimethyl imidazolium tetrafluoroborate | Fluka | 402846-78-0 | Used as received | ≥0.998 | – |
| 1-butyl-3-methyl imidazolium tetrafluoroborate | Fluka | 174501-65-6 | Used as such | ≥0.993 | – |
| 1-ethyl-3-methyl imidazolium tetrafluoroborate | Fluka | 143314-16-3 | Used as such | ≥0.990 | – |
| Cyclopentanone | Fluka | 120-92-3 | Fractional distillation | ≥0.995 | GC |
| Cyclohexanone | Fluka | 108-94-1 | Fractional distillation | ≥0.990 | GC |

*GC* gas chromatography

**Table 2** Comparison of experimental densities, $\rho$, speeds of sound, $u$, and molar heat capacities, $C_p$, values of pure components with literature values at $T = (293.15–308.15)$ K

| Components | $T$/K | $\rho$/kg m$^{-3}$ | | $u$/m s$^{-1}$ | | $C_p$/J K$^{-1}$ mol$^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | Expt. | Lit. | Expt. | Lit. | Expt. | Lit. |
| [Bmmim][$BF_4$] | 293.15 | 1193.5 | 1196.716[a] | 1659.7 | 1654.88[a] | 413.03 | – |
| | 298.15 | 1191.8 | 1191.2[b] | 1645.7 | 1641.44[a] | 416.01 | – |
| | | | 1193.338[a] | | | | |
| | | | 1193.19[c] | | | | |
| | 303.15 | 1189.7 | 1189.80[c] | 1632.5 | 1628.74[a] | 418.84 | – |
| | | | 1189.921[a] | | | | |
| | 308.15 | 1187.9 | 1186.516[a] | 1619.8 | 1616.88[a] | 421.70 | – |
| [Bmim][$BF_4$] | 293.15 | 1203.1 | 1204.6[d] | 1578.1 | 1578.0[f] | 362.35 | 362.31[u] |
| | | | 1204.16[e] | | | | 362.5[f] |
| | | | 1202.952[f] | | | | |
| | 298.15 | 1198.9 | 1198.78[g] | 1565.5 | 1565.1[f] | 365.12 | 364.8[f] |
| | | | 1199.387[f] | | 1565.09[g] | | 366.28[g] |
| | | | | | 1566[h] | | |
| | 303.15 | 1195.3 | 1195.18[g] | 1554.1 | 1554[f] | 367.48 | 367.37[u] |
| | | | 1196.98[e] | | 1555.5[f] | | 367.2[f] |
| | | | 1195.818[f] | | 1553.15[g] | | |
| | 308.15 | 1191.7 | 1192.266[f] | 1542.3 | 1542[f] | 369.88 | 369.94[u] |
| | | | 1191.60[g] | | 1540.3[f] | | 369.5[f] |
| [Emim][$BF_4$] | 293.15 | 1283.9 | 1284[i] | 1631.1 | 1631.1[m] | 303.20 | 303.23[v] |
| | 298.15 | 1279.9 | 1280[i] | 1619.2 | 1622.89 [k] | 304.53 | 304.87[v] |
| | | | 1280.07[j] | | 1629 [l] | | |
| | 303.15 | 1276.3 | 1276[i] | 1607.4 | 1608.1[m] | 306.29 | 306.58[v] |
| | 308.15 | 1272.1 | 1272[i] | 1596.2 | 1599.47 [k] | 308.03 | 308.36[v] |
| | | | 1272.48[j] | | 1606 [l] | | |
| Cyclopentanone | 293.15 | 949.3 | 949.34[m] | 1414.6 | 1414.3[m] | 152.95 | 152.99[m] |
| | 298.15 | 944.5 | 944.52[m] | 1393.6 | 1393.2[m] | 154.45 | 154.69[m] |
| | | | 944.35[n] | | 1394.1[p] | | 154.5[w] |
| | | | 945.3[o] | | | | |
| | 303.15 | 939.7 | 939.68[m] | 1372.6 | 1372.5[m] | 155.61 | 155.74[m] |
| | 308.15 | 934.8 | 934.84[m] | 1352.2 | 1352.6[m] | 156.76 | 156.81[m] |
| | | | 934.69[n] | | | | |
| Cyclohexanone | 293.15 | 947.4 | 947.39[m] | 1431.2 | 1430.5[q] | 176.17 | 176.19[m] |
| | | | 947.80[r] | | 1431.9[m] | | |
| | 298.15 | 942.9 | 942.90[m] | 1414.5 | 1408.0[p] | 178.27 | 178.37[m] |
| | | | 942.76[s] | | 1414.8[m] | | 177.97[x] |
| | 303.15 | 938.1 | 938.05[m] | 1395.1 | 1395.6[m] | 180.38 | 180.46[m] |
| | | | 940.3[t] | | | | |
| | 308.15 | 933.2 | 933.18[m] | 1375.1 | 1375.8[m] | 182.46 | 182.39[m] |
| | | | 933.8[s] | | | | |

Standard uncertainties, $u$, are $u$ ($T$) (DSA) = ±0.01 K; $u$ ($\rho$) = ±0.5 kg m$^{-3}$; $u$ ($u$) = ±0.5 m s$^{-1}$; $u$ ($C_p$) = ±0.8%; $u$ ($T$) (DSC) = ±0.02 K
[a] Ref. [19], [b] Ref. [20], [c] Ref. [21], [d] Ref. [22], [e] Ref. [23], [f] Ref. [24], [g] Ref. [25], [h] Ref. [26], [i] Ref. [27], [j] Ref. [28], [k] Ref. [29], [l] Ref. [30], [m] Ref. [14], [n] Ref. [31], [o] Ref. [32], [p] Ref. [33], [q] Ref. [34], [r] Ref. [35], [s] Ref. [36], [t] Ref. [37], [u] Ref. [40], [v] Ref. [41], [w] Ref. [42], [x] Ref. [43]

produced by scanning (900 s) an isothermal level at the initial and final temperature. The temperature cycle and scanning rate of isothermal level was maintained by software. After scanning, a graph between heat flow and calorimeter temperature along with $C_P$ values was displayed. The $C_P$ values of the purified liquids are

summarized in Table 2 and compared with their literature values [40–43]. The standard uncertainties of the reported $C_P$ values and temperature are estimated to be ±0.8% and ±0.02 K, respectively.

## Results

The molar heat capacities $(C_P)_{123}$ of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] or [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) ternary mixtures were measured over entire mole fraction of (1) and (2) components in temperature range of (293.15–308.15) K with 5-K interval and are listed in Table 3. The excess heat capacities, $\left(C_P^E\right)_{123}$, the difference between the molar heat capacities of the mixture and the summation of the pure components contribution were calculated for the present (1 + 2 + 3) mixtures using expression cited in the work of Lide and Kehiaian [44]:

$$\left(C_P^E\right)_{123} = (C_P)_{123} - \sum_{1=1}^{3} x_1 (C_P)_1 \quad (1)$$

where $(C_P)_{123}$, $(C_P)_1$ (1 = 1 or 2 or 3), $x_1$ (1 = 1 or 2 or 3) denote molar heat capacities of the ternary mixtures, molar heat capacities and mole fraction of pure component (1 = 1 or 2 or 3), respectively. The obtained $\left(C_P^E\right)_{123}$ values for the investigated mixtures are recorded in Table 3.

The experimental $\left(C_P^E\right)_{123}$ data at the studied temperatures were fitted to Redlich–Kister equation [45]:

$$\begin{aligned}\left(C_P^E\right)_{123} =& x_1x_2\left[\sum_{n=0}^{2}(C_P)_{12}^{(n)}(x_1-x_2)^n\right] \\ &+x_2x_3\left[\sum_{n=0}^{2}(C_P)_{23}^{(n)}(x_2-x_3)^n\right] \\ &+x_1x_3\left[\sum_{n=0}^{2}(C_P)_{13}^{(n)}(x_1-x_3)^n\right] \\ &+x_1x_2x_3\left[\sum_{n=0}^{2}(C_P)_{123}^{(n)}(x_2-x_3)^n x_1^n\right]\end{aligned} \quad (2)$$

where $x_1$, $x_2$ and $x_3$ are the mole fractions of (1), (2) and (3) components. The $(C_P)_{12}^{(n)}$, $(C_P)_{23}^{(n)}$, $(C_P)_{13}^{(n)}$, ($n$ = 0–2), are parameters of sub-binary mixtures (1 + 2), (2 + 3), (1 + 3) of (1 + 2 + 3) mixture and were taken from the literature [11–14]. The $(C_P)_{123}^{(n)}$ ($n$ = 0–2) are characteristic parameters of (1 + 2 + 3) mixture and were obtained by fitting the measured $\left(C_P^E\right)_{123}$ data to Eq. (2) by least-squares method. The quality of the fit was assessed via the standard deviation, $\left(C_P^E\right)_{123}$, expressed as:

**Table 3** Comparison of experimental, excess heat capacities $\left(C_P^E\right)_{123}$ data for the various (1 + 2 + 3) ternary mixtures with values predicted from the Graph and Flory theories at $T$ = (293.15–308.15) K

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $\left(C_P^E\right)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone (3) | | | | | |
| *T/K* = 293.15 | | | | | |
| 0.0922 | 0.7616 | 353.23 | 16.82 | 18.48 | −0.41 |
| 0.1043 | 0.7529 | 350.60 | 12.87 | 12.87 | −0.56 |
| 0.1481 | 0.7191 | 338.15 | −3.90 | −4.68 | −1.06 |
| 0.1705 | 0.7018 | 332.87 | −11.38 | −12.34 | −1.29 |
| 0.2163 | 0.6664 | 325.51 | −23.24 | −25.35 | −1.75 |
| 0.2368 | 0.6403 | 323.55 | −25.07 | −27.31 | −1.77 |
| 0.2772 | 0.5889 | 321.24 | −27.12 | −29.53 | −1.76 |
| 0.2971 | 0.5636 | 320.70 | −27.53 | −29.86 | −1.73 |
| 0.3169 | 0.5385 | 320.29 | −27.84 | −29.73 | −1.70 |
| 0.3364 | 0.5136 | 319.62 | −28.37 | −29.12 | −1.65 |
| 0.3601 | 0.4949 | 320.11 | −30.13 | −30.13 | −1.78 |
| 0.3841 | 0.4759 | 321.40 | −31.10 | −30.52 | −1.89 |
| 0.4084 | 0.4566 | 323.22 | −31.56 | −30.32 | −1.99 |
| 0.4332 | 0.4370 | 325.76 | −31.37 | −29.59 | −2.09 |
| 0.4583 | 0.4172 | 328.99 | −30.51 | −28.35 | −2.17 |
| 0.4838 | 0.3970 | 332.94 | −28.97 | −26.62 | −2.23 |
| 0.5064 | 0.3742 | 337.06 | −25.95 | −23.63 | −2.17 |
| 0.5198 | 0.3566 | 340.33 | −22.48 | −20.83 | −2.05 |
| 0.5328 | 0.3395 | 343.64 | −18.97 | −18.09 | −1.93 |
| 0.5453 | 0.3230 | 346.97 | −15.44 | −15.44 | −1.80 |
| 0.5575 | 0.3070 | 350.22 | −12.01 | −12.87 | −1.67 |
| 0.5693 | 0.2915 | 353.42 | −8.63 | −10.39 | −1.54 |
| 0.5807 | 0.2765 | 356.44 | −5.43 | −6.01 | −1.41 |
| 0.6049 | 0.2570 | 361.07 | −3.01 | −4.18 | −1.38 |
| 0.6228 | 0.2454 | 364.16 | −2.15 | −3.59 | −1.40 |
| 0.6405 | 0.2338 | 367.19 | −1.30 | −2.00 | −1.42 |
| 0.6581 | 0.2224 | 370.21 | −0.47 | −0.46 | −1.43 |
| 0.6680 | 0.2087 | 372.00 | 1.62 | 1.62 | −1.27 |
| 0.6846 | 0.1870 | 374.35 | 4.20 | 4.72 | −1.03 |
| 0.7011 | 0.1655 | 376.79 | 6.84 | 7.56 | −0.78 |
| 0.7175 | 0.1442 | 378.82 | 9.07 | 10.12 | −0.53 |
| 0.7709 | 0.1050 | 387.17 | 11.74 | 13.06 | −0.32 |
| *T/K* = 298.15 | | | | | |
| 0.0922 | 0.7616 | 357.42 | 18.41 | 20.23 | 0.01 |
| 0.1043 | 0.7529 | 354.94 | 14.60 | 14.60 | −0.11 |
| 0.1481 | 0.7191 | 342.45 | −2.23 | −2.99 | −0.52 |
| 0.1705 | 0.7018 | 337.85 | −9.04 | −10.64 | −0.71 |
| 0.2163 | 0.6664 | 329.46 | −21.95 | −23.64 | −1.09 |
| 0.2368 | 0.6403 | 327.90 | −23.38 | −25.58 | −1.07 |
| 0.2772 | 0.5889 | 325.85 | −25.17 | −27.80 | −1.00 |
| 0.2971 | 0.5636 | 324.66 | −26.24 | −28.14 | −0.96 |
| 0.3169 | 0.5385 | 324.48 | −26.31 | −28.04 | −0.91 |
| 0.3364 | 0.5136 | 324.03 | −26.61 | −27.48 | −0.84 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.3601 | 0.4949 | 324.41 | −28.49 | −28.49 | −0.95 |
| 0.3841 | 0.4759 | 325.72 | −29.45 | −28.88 | −1.05 |
| 0.4084 | 0.4566 | 327.36 | −30.10 | −28.69 | −1.14 |
| 0.4332 | 0.4370 | 329.88 | −29.94 | −27.97 | −1.23 |
| 0.4583 | 0.4172 | 333.08 | −29.13 | −26.74 | −1.30 |
| 0.4838 | 0.3970 | 337.12 | −27.51 | −25.03 | −1.36 |
| 0.5064 | 0.3742 | 341.18 | −24.56 | −22.10 | −1.32 |
| 0.5198 | 0.3566 | 344.28 | −21.26 | −19.41 | −1.20 |
| 0.5328 | 0.3395 | 347.63 | −17.70 | −16.78 | −1.09 |
| 0.5453 | 0.3230 | 350.88 | −14.24 | −14.24 | −0.97 |
| 0.5575 | 0.3070 | 354.03 | −10.91 | −11.80 | −0.86 |
| 0.5693 | 0.2915 | 357.14 | −7.63 | −9.45 | −0.74 |
| 0.5807 | 0.2765 | 360.02 | −4.57 | −5.20 | −0.63 |
| 0.6049 | 0.2570 | 364.54 | −2.27 | −3.48 | −0.62 |
| 0.6228 | 0.2454 | 367.57 | −1.47 | −2.92 | −0.66 |
| 0.6405 | 0.2338 | 370.56 | −0.67 | −1.36 | −0.69 |
| 0.6581 | 0.2224 | 373.50 | 0.06 | 0.14 | −0.72 |
| 0.6680 | 0.2087 | 375.20 | 2.06 | 2.06 | −0.59 |
| 0.6846 | 0.1870 | 377.38 | 4.47 | 4.88 | −0.38 |
| 0.7011 | 0.1655 | 379.63 | 6.93 | 7.42 | −0.17 |
| 0.7175 | 0.1442 | 381.99 | 9.49 | 9.66 | 0.04 |
| 0.7709 | 0.1050 | 390.28 | 12.07 | 12.23 | 0.15 |
| $T/K = 303.15$ | | | | | |
| 0.0922 | 0.7616 | 361.53 | 20.29 | 22.08 | 0.40 |
| 0.1043 | 0.7529 | 358.98 | 16.40 | 16.40 | 0.29 |
| 0.1481 | 0.7191 | 345.80 | −1.15 | −1.32 | −0.05 |
| 0.1705 | 0.7018 | 341.30 | −7.88 | −9.02 | −0.22 |
| 0.2163 | 0.6664 | 333.04 | −20.70 | −22.06 | −0.55 |
| 0.2368 | 0.6403 | 331.65 | −21.95 | −23.99 | −0.51 |
| 0.2772 | 0.5889 | 329.34 | −24.01 | −26.21 | −0.42 |
| 0.2971 | 0.5636 | 328.37 | −24.85 | −26.57 | −0.36 |
| 0.3169 | 0.5385 | 328.03 | −25.09 | −26.49 | −0.30 |
| 0.3364 | 0.5136 | 327.67 | −25.31 | −25.97 | −0.24 |
| 0.3601 | 0.4949 | 328.27 | −26.98 | −26.98 | −0.34 |
| 0.3841 | 0.4759 | 329.62 | −27.93 | −27.38 | −0.43 |
| 0.4084 | 0.4566 | 331.29 | −28.56 | −27.19 | −0.52 |
| 0.4332 | 0.4370 | 333.82 | −28.41 | −26.46 | −0.60 |
| 0.4583 | 0.4172 | 337.15 | −27.49 | −25.23 | −0.67 |
| 0.4838 | 0.3970 | 341.00 | −26.08 | −23.50 | −0.74 |
| 0.5064 | 0.3742 | 345.15 | −23.04 | −20.63 | −0.70 |
| 0.5198 | 0.3566 | 348.08 | −19.91 | −18.02 | −0.60 |
| 0.5328 | 0.3395 | 351.35 | −16.44 | −15.48 | −0.50 |
| 0.5453 | 0.3230 | 354.53 | −13.05 | −13.05 | −0.39 |
| 0.5575 | 0.3070 | 357.62 | −9.79 | −10.71 | −0.29 |
| 0.5693 | 0.2915 | 360.62 | −6.61 | −8.47 | −0.19 |
| 0.5807 | 0.2765 | 363.40 | −3.65 | −4.34 | −0.09 |
| 0.6049 | 0.2570 | 367.83 | −1.46 | −1.70 | −0.10 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.6228 | 0.2454 | 370.82 | −0.72 | −1.15 | −0.15 |
| 0.6405 | 0.2338 | 373.78 | 0.03 | 0.62 | −0.20 |
| 0.6581 | 0.2224 | 376.68 | 0.71 | 0.87 | −0.25 |
| 0.6680 | 0.2087 | 378.29 | 2.62 | 2.62 | −0.13 |
| 0.6846 | 0.1870 | 380.33 | 4.89 | 5.18 | 0.04 |
| 0.7011 | 0.1655 | 382.46 | 7.23 | 7.45 | 0.22 |
| 0.7175 | 0.1442 | 384.61 | 9.58 | 9.39 | 0.39 |
| 0.7709 | 0.1050 | 393.24 | 12.46 | 11.58 | 0.42 |
| $T/K = 308.15$ | | | | | |
| 0.0922 | 0.7616 | 365.07 | 21.57 | 23.37 | 0.36 |
| 0.1043 | 0.7529 | 362.57 | 17.72 | 17.72 | 0.26 |
| 0.1481 | 0.7191 | 349.41 | 0.16 | 0.11 | −0.06 |
| 0.1705 | 0.7018 | 344.39 | −7.11 | −7.53 | −0.22 |
| 0.2163 | 0.6664 | 336.60 | −19.49 | −20.45 | −0.53 |
| 0.2368 | 0.6403 | 335.10 | −20.86 | −22.34 | −0.48 |
| 0.2772 | 0.5889 | 332.89 | −22.82 | −24.52 | −0.38 |
| 0.2971 | 0.5636 | 332.47 | −23.12 | −24.89 | −0.32 |
| 0.3169 | 0.5385 | 332.06 | −23.42 | −24.83 | −0.25 |
| 0.3364 | 0.5136 | 331.67 | −23.68 | −24.33 | −0.18 |
| 0.3601 | 0.4949 | 332.32 | −25.32 | −25.32 | −0.27 |
| 0.3841 | 0.4759 | 333.70 | −26.25 | −25.69 | −0.36 |
| 0.4084 | 0.4566 | 335.55 | −26.72 | −25.48 | −0.44 |
| 0.4332 | 0.4370 | 337.94 | −26.72 | −24.74 | −0.52 |
| 0.4583 | 0.4172 | 341.24 | −25.86 | −23.50 | −0.59 |
| 0.4838 | 0.3970 | 344.92 | −24.63 | −21.77 | −0.66 |
| 0.5064 | 0.3742 | 349.16 | −21.51 | −18.96 | −0.62 |
| 0.5198 | 0.3566 | 352.06 | −18.42 | −16.45 | −0.51 |
| 0.5328 | 0.3395 | 355.19 | −15.09 | −14.02 | −0.41 |
| 0.5453 | 0.3230 | 358.37 | −11.69 | −11.69 | −0.31 |
| 0.5575 | 0.3070 | 361.42 | −8.48 | −9.47 | −0.21 |
| 0.5693 | 0.2915 | 364.28 | −5.44 | −6.35 | −0.11 |
| 0.5807 | 0.2765 | 366.95 | −2.58 | −3.34 | −0.01 |
| 0.6049 | 0.2570 | 371.28 | −0.51 | −0.59 | −0.02 |
| 0.6228 | 0.2454 | 374.23 | 0.17 | 0.27 | −0.08 |
| 0.6405 | 0.2338 | 377.14 | 0.86 | 0.64 | −0.12 |
| 0.6581 | 0.2224 | 379.99 | 1.47 | 1.69 | −0.17 |
| 0.6680 | 0.2087 | 381.51 | 3.29 | 3.29 | −0.06 |
| 0.6846 | 0.1870 | 383.36 | 5.37 | 5.60 | 0.11 |
| 0.7011 | 0.1655 | 385.34 | 7.56 | 7.59 | 0.28 |
| 0.7175 | 0.1442 | 387.40 | 9.81 | 9.25 | 0.45 |
| 0.7709 | 0.1050 | 395.97 | 12.59 | 11.09 | 0.46 |
| [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclohexanone (3) | | | | | |
| $T/K = 293.15$ | | | | | |
| 0.0846 | 0.7861 | 373.31 | 30.75 | 31.76 | −0.01 |
| 0.1064 | 0.7686 | 363.32 | 18.85 | 19.97 | −0.26 |
| 0.1286 | 0.7509 | 355.30 | 8.87 | 8.87 | −0.51 |
| 0.1510 | 0.7330 | 347.10 | −1.30 | −1.34 | −0.76 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.1737 | 0.7148 | 340.84 | −9.55 | −10.68 | −1.00 |
| 0.2200 | 0.6777 | 331.25 | −23.20 | −25.82 | −1.47 |
| 0.2411 | 0.6517 | 329.72 | −24.89 | −26.09 | −1.52 |
| 0.2826 | 0.6004 | 328.73 | −26.16 | −28.53 | −1.57 |
| 0.3032 | 0.5750 | 328.25 | −26.79 | −27.88 | −1.58 |
| 0.3236 | 0.5498 | 328.49 | −26.68 | −26.68 | −1.58 |
| 0.3677 | 0.5054 | 329.02 | −28.34 | −27.12 | −1.69 |
| 0.4165 | 0.4656 | 331.32 | −30.19 | −29.30 | −1.92 |
| 0.4413 | 0.4453 | 333.94 | −29.66 | −29.41 | −2.01 |
| 0.4666 | 0.4247 | 337.42 | −28.34 | −28.96 | −2.09 |
| 0.4921 | 0.4039 | 341.41 | −26.52 | −27.96 | −2.16 |
| 0.5152 | 0.3807 | 345.51 | −23.57 | −24.62 | −2.12 |
| 0.5292 | 0.3630 | 348.26 | −20.84 | −20.84 | −2.01 |
| 0.5427 | 0.3458 | 351.33 | −17.76 | −17.15 | −1.90 |
| 0.5558 | 0.3292 | 354.59 | −14.51 | −13.63 | −1.79 |
| 0.5685 | 0.3131 | 357.81 | −11.31 | −10.27 | −1.68 |
| 0.5808 | 0.2974 | 360.95 | −8.16 | −7.03 | −1.57 |
| 0.5928 | 0.2822 | 364.03 | −5.09 | −3.99 | −1.45 |
| 0.6171 | 0.2622 | 368.88 | −2.27 | −1.77 | −1.42 |
| 0.6347 | 0.2501 | 372.07 | −0.99 | −0.93 | −1.43 |
| 0.6522 | 0.2381 | 375.20 | 0.22 | 0.24 | −1.44 |
| 0.6695 | 0.2263 | 378.23 | 1.35 | 1.08 | −1.44 |
| 0.6800 | 0.2124 | 380.24 | 3.46 | 3.46 | −1.30 |
| 0.6974 | 0.1905 | 383.03 | 6.20 | 7.11 | −1.07 |
| 0.7148 | 0.1687 | 385.79 | 8.90 | 10.22 | −0.84 |
| 0.7320 | 0.1471 | 389.34 | 12.40 | 12.70 | −0.61 |
| 0.7563 | 0.1268 | 394.28 | 15.37 | 13.59 | −0.47 |
| 0.7848 | 0.1069 | 397.93 | 15.97 | 13.53 | −0.38 |
| $T/K = 298.15$ | | | | | |
| 0.0846 | 0.7861 | 376.36 | 31.09 | 31.36 | 0.54 |
| 0.1064 | 0.7686 | 366.32 | 19.14 | 19.94 | 0.34 |
| 0.1286 | 0.7509 | 358.35 | 9.20 | 9.20 | 0.13 |
| 0.1510 | 0.7330 | 350.48 | −0.65 | −0.67 | −0.08 |
| 0.1737 | 0.7148 | 343.87 | −9.26 | −9.70 | −0.28 |
| 0.2200 | 0.6777 | 335.46 | −21.74 | −23.30 | −0.67 |
| 0.2411 | 0.6517 | 334.75 | −22.61 | −24.52 | −0.69 |
| 0.2826 | 0.6004 | 333.72 | −23.92 | −24.93 | −0.68 |
| 0.3032 | 0.5750 | 333.23 | −24.56 | −26.30 | −0.67 |
| 0.3236 | 0.5498 | 332.79 | −25.15 | −25.15 | −0.64 |
| 0.3677 | 0.5054 | 333.31 | −26.81 | −25.59 | −0.73 |
| 0.4165 | 0.4656 | 335.63 | −28.66 | −27.72 | −0.94 |
| 0.4413 | 0.4453 | 338.21 | −28.18 | −27.83 | −1.03 |
| 0.4666 | 0.4247 | 341.61 | −26.94 | −27.41 | −1.11 |
| 0.4921 | 0.4039 | 345.41 | −25.32 | −26.45 | −1.18 |
| 0.5152 | 0.3807 | 349.51 | −22.38 | −23.25 | −1.15 |
| 0.5292 | 0.3630 | 352.28 | −19.63 | −19.63 | −1.05 |
| 0.5427 | 0.3458 | 355.23 | −16.67 | −16.10 | −0.96 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.5558 | 0.3292 | 358.29 | −13.62 | −12.74 | −0.86 |
| 0.5685 | 0.3131 | 361.39 | −10.54 | −9.53 | −0.76 |
| 0.5808 | 0.2974 | 364.41 | −7.51 | −6.44 | −0.66 |
| 0.5928 | 0.2822 | 367.39 | −4.54 | −3.55 | −0.56 |
| 0.6171 | 0.2622 | 372.07 | −1.90 | −1.44 | −0.56 |
| 0.6347 | 0.2501 | 375.20 | −0.70 | −0.64 | −0.59 |
| 0.6522 | 0.2381 | 378.25 | 0.44 | 0.39 | −0.62 |
| 0.6695 | 0.2263 | 381.21 | 1.48 | 1.02 | −0.65 |
| 0.6800 | 0.2124 | 383.13 | 3.51 | 3.51 | −0.53 |
| 0.6974 | 0.1905 | 385.80 | 6.14 | 6.95 | −0.34 |
| 0.7148 | 0.1687 | 388.74 | 9.01 | 9.85 | −0.15 |
| 0.7320 | 0.1471 | 391.92 | 12.14 | 12.14 | 0.04 |
| 0.7563 | 0.1268 | 396.76 | 14.99 | 12.92 | 0.12 |
| 0.7848 | 0.1069 | 400.19 | 15.37 | 12.80 | 0.15 |
| $T/K = 303.15$ | | | | | |
| 0.0846 | 0.7861 | 380.47 | 32.84 | 31.00 | 1.04 |
| 0.1064 | 0.7686 | 370.10 | 20.54 | 20.03 | 0.86 |
| 0.1286 | 0.7509 | 361.26 | 9.72 | 9.72 | 0.67 |
| 0.1510 | 0.7330 | 353.76 | 0.23 | 0.25 | 0.49 |
| 0.1737 | 0.7148 | 346.67 | −8.87 | −8.40 | 0.31 |
| 0.2200 | 0.6777 | 339.31 | −20.33 | −21.32 | −0.04 |
| 0.2411 | 0.6517 | 338.77 | −21.04 | −22.44 | −0.03 |
| 0.2826 | 0.6004 | 338.09 | −22.01 | −24.77 | 0.01 |
| 0.3032 | 0.5750 | 337.99 | −22.27 | −24.15 | 0.04 |
| 0.3236 | 0.5498 | 337.39 | −23.02 | −23.02 | 0.08 |
| 0.3677 | 0.5054 | 338.27 | −24.35 | −23.42 | 0.01 |
| 0.4165 | 0.4656 | 340.63 | −26.18 | −25.40 | −0.20 |
| 0.4413 | 0.4453 | 343.32 | −25.61 | −25.48 | −0.29 |
| 0.4666 | 0.4247 | 346.42 | −24.69 | −25.06 | −0.38 |
| 0.4921 | 0.4039 | 350.36 | −22.94 | −24.11 | −0.46 |
| 0.5152 | 0.3807 | 354.11 | −20.36 | −21.05 | −0.44 |
| 0.5292 | 0.3630 | 356.87 | −17.62 | −17.62 | −0.35 |
| 0.5427 | 0.3458 | 359.62 | −14.87 | −14.28 | −0.27 |
| 0.5558 | 0.3292 | 362.63 | −11.88 | −11.10 | −0.18 |
| 0.5685 | 0.3131 | 365.53 | −9.00 | −8.07 | −0.10 |
| 0.5808 | 0.2974 | 368.48 | −6.04 | −5.17 | −0.01 |
| 0.5928 | 0.2822 | 371.26 | −3.28 | −2.46 | 0.07 |
| 0.6171 | 0.2622 | 375.78 | −0.81 | −0.78 | 0.05 |
| 0.6347 | 0.2501 | 378.80 | 0.27 | 0.27 | 0.02 |
| 0.6522 | 0.2381 | 381.75 | 1.30 | 1.06 | −0.05 |
| 0.6695 | 0.2263 | 384.62 | 2.25 | 1.84 | −0.09 |
| 0.6800 | 0.2124 | 386.42 | 4.15 | 4.15 | 0.01 |
| 0.6974 | 0.1905 | 388.89 | 6.56 | 7.28 | 0.16 |
| 0.7148 | 0.1687 | 391.58 | 9.19 | 9.89 | 0.31 |
| 0.7320 | 0.1471 | 394.40 | 11.94 | 11.90 | 0.47 |
| 0.7563 | 0.1268 | 398.99 | 14.54 | 12.51 | 0.51 |
| 0.7848 | 0.1069 | 402.85 | 15.33 | 12.29 | 0.49 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| *T/K* = 308.15 | | | | | |
| 0.0846 | 0.7861 | 383.50 | 33.47 | 30.69 | 1.12 |
| 0.1064 | 0.7686 | 373.54 | 21.57 | 20.14 | 0.94 |
| 0.1286 | 0.7509 | 364.18 | 10.22 | 10.22 | 0.77 |
| 0.1510 | 0.7330 | 357.03 | 1.07 | 1.12 | 0.59 |
| 0.1737 | 0.7148 | 350.44 | −7.54 | −7.20 | 0.42 |
| 0.2200 | 0.6777 | 344.06 | −18.05 | −20.54 | 0.09 |
| 0.2411 | 0.6517 | 343.26 | −19.02 | −21.59 | 0.11 |
| 0.2826 | 0.6004 | 342.48 | −20.12 | −22.84 | 0.16 |
| 0.3032 | 0.5750 | 342.05 | −20.71 | −22.22 | 0.20 |
| 0.3236 | 0.5498 | 341.81 | −21.12 | −21.12 | 0.24 |
| 0.3677 | 0.5054 | 343.17 | −21.98 | −21.48 | 0.18 |
| 0.4165 | 0.4656 | 345.43 | −23.94 | −23.42 | −0.02 |
| 0.4413 | 0.4453 | 347.96 | −23.54 | −23.50 | −0.11 |
| 0.4666 | 0.4247 | 351.00 | −22.68 | −23.11 | −0.20 |
| 0.4921 | 0.4039 | 354.86 | −21.03 | −22.22 | −0.28 |
| 0.5152 | 0.3807 | 358.51 | −18.56 | −19.29 | −0.26 |
| 0.5292 | 0.3630 | 361.10 | −16.00 | −16.00 | −0.17 |
| 0.5427 | 0.3458 | 363.91 | −13.19 | −12.80 | −0.09 |
| 0.5558 | 0.3292 | 366.67 | −10.46 | −9.76 | −0.01 |
| 0.5685 | 0.3131 | 369.55 | −7.59 | −6.87 | 0.08 |
| 0.5808 | 0.2974 | 372.31 | −4.84 | −4.10 | 0.16 |
| 0.5928 | 0.2822 | 375.00 | −2.18 | −1.51 | 0.25 |
| 0.6171 | 0.2622 | 379.36 | 0.12 | 0.15 | 0.22 |
| 0.6347 | 0.2501 | 382.29 | 1.11 | 1.05 | 0.17 |
| 0.6522 | 0.2381 | 385.17 | 2.05 | 1.77 | 0.12 |
| 0.6695 | 0.2263 | 387.95 | 2.91 | 2.50 | 0.07 |
| 0.6800 | 0.2124 | 389.63 | 4.68 | 4.68 | 0.16 |
| 0.6974 | 0.1905 | 391.96 | 6.95 | 7.64 | 0.31 |
| 0.7148 | 0.1687 | 394.67 | 9.58 | 10.08 | 0.46 |
| 0.7320 | 0.1471 | 397.51 | 12.36 | 11.93 | 0.61 |
| 0.7563 | 0.1268 | 401.24 | 14.08 | 12.44 | 0.64 |
| 0.7848 | 0.1069 | 405.51 | 15.26 | 12.15 | 0.61 |
| [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone (3) | | | | | |
| *T/K* = 293.15 | | | | | |
| 0.0814 | 0.7865 | 300.34 | 8.05 | 8.27 | 1.37 |
| 0.1108 | 0.7626 | 310.41 | 14.06 | 13.65 | 1.21 |
| 0.1305 | 0.7471 | 316.47 | 17.33 | 16.94 | 1.10 |
| 0.1506 | 0.7313 | 323.45 | 21.46 | 20.04 | 0.99 |
| 0.1710 | 0.7151 | 327.77 | 22.91 | 22.91 | 0.88 |
| 0.1908 | 0.6949 | 331.62 | 24.63 | 25.19 | 0.83 |
| 0.2107 | 0.6745 | 335.29 | 26.20 | 27.20 | 0.78 |
| 0.2308 | 0.6539 | 338.65 | 27.42 | 28.96 | 0.73 |
| 0.2511 | 0.6332 | 341.98 | 28.58 | 30.47 | 0.69 |
| 0.2700 | 0.6089 | 344.98 | 30.33 | 31.33 | 0.71 |
| 0.3078 | 0.5605 | 350.71 | 33.49 | 32.38 | 0.75 |
| 0.3265 | 0.5364 | 353.19 | 34.73 | 32.54 | 0.78 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.3491 | 0.5181 | 355.68 | 34.09 | 33.08 | 0.70 |
| 0.3721 | 0.4994 | 358.12 | 33.36 | 33.36 | 0.62 |
| 0.3956 | 0.4803 | 360.53 | 32.53 | 33.36 | 0.54 |
| 0.4195 | 0.4608 | 362.56 | 31.27 | 33.10 | 0.46 |
| 0.4661 | 0.4183 | 366.01 | 28.99 | 31.50 | 0.39 |
| 0.4885 | 0.3954 | 367.31 | 27.90 | 30.20 | 0.39 |
| 0.5048 | 0.3800 | 368.25 | 26.92 | 29.23 | 0.38 |
| 0.5179 | 0.3628 | 368.96 | 26.80 | 27.98 | 0.43 |
| 0.5306 | 0.3460 | 369.63 | 26.70 | 26.70 | 0.49 |
| 0.5430 | 0.3297 | 370.01 | 26.30 | 25.39 | 0.54 |
| 0.5551 | 0.3138 | 370.71 | 26.24 | 24.06 | 0.60 |
| 0.5669 | 0.2983 | 371.34 | 26.13 | 22.72 | 0.66 |
| 0.5914 | 0.2780 | 372.24 | 23.71 | 20.82 | 0.63 |
| 0.6092 | 0.2658 | 372.79 | 21.46 | 19.60 | 0.58 |
| 0.6270 | 0.2538 | 373.15 | 19.00 | 18.36 | 0.52 |
| 0.6446 | 0.2417 | 373.40 | 16.49 | 17.08 | 0.48 |
| 0.6552 | 0.2273 | 373.14 | 15.64 | 15.64 | 0.55 |
| 0.6730 | 0.2043 | 372.83 | 14.15 | 13.30 | 0.66 |
| 0.7085 | 0.1585 | 371.83 | 10.80 | 8.57 | 0.89 |
| 0.7340 | 0.1371 | 370.63 | 6.18 | 6.32 | 0.91 |
| *T/K* = 298.15 | | | | | |
| 0.0814 | 0.7865 | 302.40 | 8.62 | 7.22 | 1.55 |
| 0.1108 | 0.7626 | 312.74 | 14.86 | 13.46 | 1.44 |
| 0.1305 | 0.7471 | 319.23 | 18.52 | 17.28 | 1.35 |
| 0.1506 | 0.7313 | 326.12 | 22.53 | 20.85 | 1.27 |
| 0.1710 | 0.7151 | 330.64 | 24.14 | 24.14 | 1.18 |
| 0.1908 | 0.6949 | 334.54 | 25.90 | 26.73 | 1.15 |
| 0.2107 | 0.6745 | 338.54 | 27.75 | 29.00 | 1.12 |
| 0.2308 | 0.6539 | 342.08 | 29.12 | 30.98 | 1.10 |
| 0.2511 | 0.6332 | 345.75 | 30.60 | 32.67 | 1.07 |
| 0.2700 | 0.6089 | 348.74 | 32.29 | 33.63 | 1.11 |
| 0.3078 | 0.5605 | 354.51 | 35.43 | 34.79 | 1.19 |
| 0.3265 | 0.5364 | 357.24 | 36.89 | 34.99 | 1.23 |
| 0.3491 | 0.5181 | 360.05 | 36.54 | 35.59 | 1.16 |
| 0.3721 | 0.4994 | 362.61 | 35.88 | 35.88 | 1.10 |
| 0.3956 | 0.4803 | 364.93 | 34.93 | 35.86 | 1.03 |
| 0.4195 | 0.4608 | 366.86 | 33.53 | 35.53 | 0.96 |
| 0.4661 | 0.4183 | 370.52 | 31.37 | 33.69 | 0.90 |
| 0.4885 | 0.3954 | 371.76 | 30.19 | 32.26 | 0.90 |
| 0.5048 | 0.3800 | 372.67 | 29.15 | 31.17 | 0.89 |
| 0.5179 | 0.3628 | 373.26 | 28.90 | 29.86 | 0.94 |
| 0.5306 | 0.3460 | 373.68 | 28.52 | 28.52 | 1.00 |
| 0.5430 | 0.3297 | 374.09 | 28.13 | 27.16 | 1.06 |
| 0.5551 | 0.3138 | 374.41 | 27.67 | 25.79 | 1.12 |
| 0.5669 | 0.2983 | 374.88 | 27.38 | 24.41 | 1.17 |
| 0.5914 | 0.2780 | 375.74 | 24.88 | 22.35 | 1.14 |
| 0.6092 | 0.2658 | 376.07 | 22.39 | 20.97 | 1.08 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.6270 | 0.2538 | 376.45 | 19.91 | 19.57 | 1.02 |
| 0.6446 | 0.2417 | 376.80 | 17.47 | 18.12 | 0.96 |
| 0.6552 | 0.2273 | 376.65 | 16.71 | 16.71 | 1.03 |
| 0.6730 | 0.2043 | 376.33 | 15.19 | 14.44 | 1.13 |
| 0.7085 | 0.1585 | 374.93 | 11.38 | 10.00 | 1.35 |
| 0.7340 | 0.1371 | 373.89 | 6.88 | 7.78 | 1.34 |
| *T/K* = 303.15 | | | | | |
| 0.0814 | 0.7865 | 304.98 | 9.43 | 8.59 | 1.64 |
| 0.1108 | 0.7626 | 315.27 | 15.59 | 14.68 | 1.52 |
| 0.1305 | 0.7471 | 321.75 | 19.22 | 18.40 | 1.43 |
| 0.1506 | 0.7313 | 328.84 | 23.39 | 21.88 | 1.34 |
| 0.1710 | 0.7151 | 333.46 | 25.08 | 25.08 | 1.25 |
| 0.1908 | 0.6949 | 337.44 | 26.89 | 27.64 | 1.22 |
| 0.2107 | 0.6745 | 341.51 | 28.81 | 29.90 | 1.19 |
| 0.2308 | 0.6539 | 345.13 | 30.24 | 31.87 | 1.16 |
| 0.2511 | 0.6332 | 348.89 | 31.77 | 33.56 | 1.14 |
| 0.2700 | 0.6089 | 351.92 | 33.49 | 34.57 | 1.18 |
| 0.3078 | 0.5605 | 357.75 | 36.66 | 35.87 | 1.26 |
| 0.3265 | 0.5364 | 360.53 | 38.15 | 36.13 | 1.31 |
| 0.3491 | 0.5181 | 363.40 | 37.83 | 36.73 | 1.23 |
| 0.3721 | 0.4994 | 365.82 | 37.01 | 37.01 | 1.16 |
| 0.3956 | 0.4803 | 368.21 | 36.10 | 37.00 | 1.09 |
| 0.4195 | 0.4608 | 370.36 | 34.90 | 36.67 | 1.02 |
| 0.4661 | 0.4183 | 373.90 | 32.57 | 34.92 | 0.95 |
| 0.4885 | 0.3954 | 375.32 | 31.55 | 33.55 | 0.96 |
| 0.5048 | 0.3800 | 376.40 | 30.65 | 32.51 | 0.95 |
| 0.5179 | 0.3628 | 376.97 | 30.36 | 31.26 | 1.01 |
| 0.5306 | 0.3460 | 377.40 | 29.98 | 29.98 | 1.07 |
| 0.5430 | 0.3297 | 378.02 | 29.80 | 28.69 | 1.13 |
| 0.5551 | 0.3138 | 378.58 | 29.57 | 27.38 | 1.19 |
| 0.5669 | 0.2983 | 378.98 | 29.20 | 26.05 | 1.25 |
| 0.5914 | 0.2780 | 379.86 | 26.69 | 24.01 | 1.22 |
| 0.6092 | 0.2658 | 380.35 | 24.33 | 22.64 | 1.16 |
| 0.6270 | 0.2538 | 380.84 | 21.94 | 21.23 | 1.09 |
| 0.6446 | 0.2417 | 381.11 | 19.40 | 19.78 | 1.04 |
| 0.6552 | 0.2273 | 380.73 | 18.40 | 18.40 | 1.11 |
| 0.6730 | 0.2043 | 380.43 | 16.88 | 16.17 | 1.22 |
| 0.7085 | 0.1585 | 378.77 | 12.78 | 11.76 | 1.44 |
| 0.7340 | 0.1371 | 377.74 | 8.26 | 9.50 | 1.44 |
| *T/K* = 308.15 | | | | | |
| 0.0814 | 0.7865 | 306.97 | 9.67 | 7.99 | 1.72 |
| 0.1108 | 0.7626 | 317.70 | 16.23 | 14.92 | 1.60 |
| 0.1305 | 0.7471 | 325.23 | 20.88 | 19.12 | 1.51 |
| 0.1506 | 0.7313 | 331.05 | 23.77 | 23.02 | 1.42 |
| 0.1710 | 0.7151 | 336.82 | 26.58 | 26.58 | 1.34 |
| 0.1908 | 0.6949 | 341.02 | 28.59 | 29.41 | 1.31 |
| 0.2107 | 0.6745 | 345.33 | 30.71 | 31.90 | 1.28 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.2308 | 0.6539 | 349.15 | 32.33 | 34.07 | 1.25 |
| 0.2511 | 0.6332 | 353.12 | 34.05 | 35.92 | 1.23 |
| 0.2700 | 0.6089 | 356.32 | 35.91 | 37.11 | 1.27 |
| 0.3078 | 0.5605 | 362.42 | 39.33 | 38.71 | 1.36 |
| 0.3265 | 0.5364 | 365.08 | 40.67 | 39.13 | 1.41 |
| 0.3491 | 0.5181 | 368.28 | 40.66 | 39.71 | 1.34 |
| 0.3721 | 0.4994 | 370.81 | 39.92 | 39.92 | 1.27 |
| 0.3956 | 0.4803 | 373.29 | 39.06 | 39.79 | 1.20 |
| 0.4195 | 0.4608 | 375.66 | 38.05 | 39.30 | 1.13 |
| 0.4661 | 0.4183 | 378.99 | 35.47 | 37.26 | 1.06 |
| 0.4885 | 0.3954 | 380.33 | 34.33 | 35.84 | 1.07 |
| 0.5048 | 0.3800 | 381.34 | 33.35 | 34.70 | 1.06 |
| 0.5179 | 0.3628 | 381.78 | 32.92 | 33.60 | 1.12 |
| 0.5306 | 0.3460 | 382.16 | 32.48 | 32.48 | 1.18 |
| 0.5430 | 0.3297 | 382.66 | 32.16 | 31.36 | 1.24 |
| 0.5551 | 0.3138 | 383.15 | 31.85 | 30.23 | 1.31 |
| 0.5669 | 0.2983 | 383.58 | 31.50 | 29.11 | 1.37 |
| 0.5914 | 0.2780 | 384.48 | 28.98 | 26.95 | 1.33 |
| 0.6092 | 0.2658 | 385.01 | 26.64 | 25.36 | 1.27 |
| 0.6270 | 0.2538 | 385.53 | 24.26 | 23.71 | 1.20 |
| 0.6446 | 0.2417 | 385.86 | 21.76 | 22.03 | 1.14 |
| 0.6552 | 0.2273 | 385.73 | 21.00 | 21.00 | 1.22 |
| 0.6730 | 0.2043 | 385.33 | 19.36 | 19.32 | 1.33 |
| 0.7085 | 0.1585 | 383.48 | 15.03 | 16.27 | 1.56 |
| 0.7340 | 0.1371 | 382.27 | 10.30 | 14.32 | 1.56 |
| [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclohexanone (3) | | | | | |
| *T/K* = 293.15 | | | | | |
| 0.0959 | 0.7916 | 309.47 | 10.03 | 11.64 | 1.72 |
| 0.1161 | 0.7751 | 313.75 | 11.62 | 12.91 | 1.61 |
| 0.1576 | 0.7413 | 321.69 | 14.02 | 14.47 | 1.36 |
| 0.1780 | 0.7204 | 324.89 | 15.05 | 15.05 | 1.30 |
| 0.1986 | 0.6994 | 328.06 | 16.00 | 15.59 | 1.24 |
| 0.2194 | 0.6781 | 331.00 | 16.72 | 16.10 | 1.18 |
| 0.2404 | 0.6567 | 333.79 | 17.26 | 16.56 | 1.12 |
| 0.2603 | 0.6320 | 336.22 | 18.11 | 17.22 | 1.13 |
| 0.2801 | 0.6073 | 338.67 | 19.01 | 17.81 | 1.14 |
| 0.2999 | 0.5827 | 341.06 | 19.84 | 18.33 | 1.16 |
| 0.3197 | 0.5581 | 343.53 | 20.74 | 18.77 | 1.17 |
| 0.3429 | 0.5387 | 346.02 | 20.20 | 18.76 | 1.07 |
| 0.3664 | 0.5191 | 348.27 | 19.38 | 18.71 | 0.98 |
| 0.3904 | 0.4990 | 350.66 | 18.63 | 18.63 | 0.88 |
| 0.4149 | 0.4786 | 352.79 | 17.55 | 18.50 | 0.79 |
| 0.4398 | 0.4577 | 355.06 | 16.57 | 18.34 | 0.70 |
| 0.4628 | 0.4343 | 357.26 | 16.30 | 18.24 | 0.68 |
| 0.5030 | 0.3945 | 361.00 | 15.58 | 17.86 | 0.65 |
| 0.5171 | 0.3767 | 362.53 | 16.03 | 17.72 | 0.70 |
| 0.5307 | 0.3594 | 363.91 | 16.38 | 17.53 | 0.74 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_p)_{123}$/J K$^{-1}$ mol$^{-1}$ | $(C_P^E)_{123}$/J K$^{-1}$ mol$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.5441 | 0.3426 | 365.29 | 16.72 | 17.28 | 0.79 |
| 0.5571 | 0.3261 | 366.67 | 17.12 | 16.99 | 0.84 |
| 0.5697 | 0.3101 | 367.86 | 17.36 | 16.66 | 0.89 |
| 0.5948 | 0.2889 | 369.70 | 15.95 | 15.95 | 0.84 |
| 0.6128 | 0.2760 | 370.99 | 14.61 | 15.43 | 0.78 |
| 0.6307 | 0.2632 | 372.33 | 13.34 | 14.90 | 0.72 |
| 0.6599 | 0.2357 | 374.48 | 12.06 | 13.82 | 0.73 |
| 0.6789 | 0.2120 | 375.86 | 11.96 | 12.83 | 0.82 |
| 0.6979 | 0.1883 | 377.06 | 11.67 | 11.67 | 0.92 |
| 0.7169 | 0.1647 | 377.95 | 11.05 | 10.32 | 1.01 |
| 0.7428 | 0.1424 | 379.55 | 9.35 | 8.85 | 1.01 |
| 0.7730 | 0.1203 | 381.88 | 7.33 | 7.29 | 0.97 |
| $T/K = 298.15$ | | | | | |
| 0.0959 | 0.7916 | 312.02 | 11.00 | 12.51 | 1.96 |
| 0.1161 | 0.7751 | 316.53 | 12.79 | 13.95 | 1.87 |
| 0.1576 | 0.7413 | 324.58 | 15.24 | 15.81 | 1.68 |
| 0.1780 | 0.7204 | 328.05 | 16.50 | 16.50 | 1.64 |
| 0.1986 | 0.6994 | 331.18 | 17.39 | 17.15 | 1.60 |
| 0.2194 | 0.6781 | 334.33 | 18.28 | 17.75 | 1.56 |
| 0.2404 | 0.6567 | 337.24 | 18.90 | 18.30 | 1.53 |
| 0.2603 | 0.6320 | 339.76 | 19.81 | 19.02 | 1.56 |
| 0.2801 | 0.6073 | 342.30 | 20.77 | 19.66 | 1.59 |
| 0.2999 | 0.5827 | 344.89 | 21.75 | 20.21 | 1.62 |
| 0.3197 | 0.5581 | 347.31 | 22.57 | 20.67 | 1.65 |
| 0.3429 | 0.5387 | 349.77 | 21.96 | 20.69 | 1.57 |
| 0.3664 | 0.5191 | 352.21 | 21.29 | 20.66 | 1.48 |
| 0.3904 | 0.4990 | 354.67 | 20.58 | 20.58 | 1.40 |
| 0.4149 | 0.4786 | 356.94 | 19.60 | 20.44 | 1.31 |
| 0.4398 | 0.4577 | 359.05 | 18.44 | 20.25 | 1.23 |
| 0.4628 | 0.4343 | 361.26 | 18.13 | 20.10 | 1.22 |
| 0.5030 | 0.3945 | 365.04 | 17.37 | 19.62 | 1.19 |
| 0.5171 | 0.3767 | 366.44 | 17.67 | 19.42 | 1.24 |
| 0.5307 | 0.3594 | 367.92 | 18.10 | 19.18 | 1.28 |
| 0.5441 | 0.3426 | 369.15 | 18.27 | 18.87 | 1.33 |
| 0.5571 | 0.3261 | 370.47 | 18.58 | 18.52 | 1.38 |
| 0.5697 | 0.3101 | 371.51 | 18.65 | 18.13 | 1.43 |
| 0.5948 | 0.2889 | 373.47 | 17.32 | 17.32 | 1.37 |
| 0.6128 | 0.2760 | 374.67 | 15.87 | 16.74 | 1.30 |
| 0.6307 | 0.2632 | 376.01 | 14.57 | 16.14 | 1.24 |
| 0.6599 | 0.2357 | 378.09 | 13.18 | 14.93 | 1.23 |
| 0.6789 | 0.2120 | 379.39 | 12.95 | 13.82 | 1.31 |
| 0.6979 | 0.1883 | 380.51 | 12.55 | 12.55 | 1.39 |
| 0.7169 | 0.1647 | 381.26 | 11.76 | 11.08 | 1.47 |
| 0.7428 | 0.1424 | 382.92 | 10.08 | 9.49 | 1.45 |
| 0.7730 | 0.1203 | 385.21 | 7.97 | 7.80 | 1.37 |
| $T/K = 303.15$ | | | | | |
| 0.0959 | 0.7916 | 314.76 | 11.84 | 12.19 | 2.15 |
| 0.1161 | 0.7751 | 319.32 | 13.66 | 14.75 | 2.05 |
| 0.1576 | 0.7413 | 327.57 | 16.28 | 16.82 | 1.84 |
| 0.1780 | 0.7204 | 331.14 | 17.61 | 17.61 | 1.79 |
| 0.1986 | 0.6994 | 334.36 | 18.56 | 18.33 | 1.75 |
| 0.2194 | 0.6781 | 337.59 | 19.52 | 19.01 | 1.71 |
| 0.2404 | 0.6567 | 340.49 | 20.10 | 19.62 | 1.67 |
| 0.2603 | 0.6320 | 343.18 | 21.15 | 20.39 | 1.70 |
| 0.2801 | 0.6073 | 345.78 | 22.15 | 21.07 | 1.74 |
| 0.2999 | 0.5827 | 348.43 | 23.17 | 21.66 | 1.77 |
| 0.3197 | 0.5581 | 350.90 | 24.02 | 22.15 | 1.81 |
| 0.3429 | 0.5387 | 353.40 | 23.43 | 22.19 | 1.71 |
| 0.3664 | 0.5191 | 355.89 | 22.78 | 22.16 | 1.62 |
| 0.3904 | 0.4990 | 358.38 | 22.08 | 22.08 | 1.53 |
| 0.4149 | 0.4786 | 360.69 | 21.11 | 21.93 | 1.43 |
| 0.4398 | 0.4577 | 362.82 | 19.93 | 21.71 | 1.34 |
| 0.4628 | 0.4343 | 365.12 | 19.70 | 21.54 | 1.33 |
| 0.5030 | 0.3945 | 368.80 | 18.81 | 20.99 | 1.29 |
| 0.5171 | 0.3767 | 370.26 | 19.15 | 20.77 | 1.34 |
| 0.5307 | 0.3594 | 371.63 | 19.45 | 20.50 | 1.40 |
| 0.5441 | 0.3426 | 372.83 | 19.57 | 20.17 | 1.44 |
| 0.5571 | 0.3261 | 374.12 | 19.84 | 19.79 | 1.50 |
| 0.5697 | 0.3101 | 375.13 | 19.86 | 19.37 | 1.55 |
| 0.5948 | 0.2889 | 377.09 | 18.50 | 18.50 | 1.49 |
| 0.6128 | 0.2760 | 378.27 | 17.01 | 17.86 | 1.41 |
| 0.6307 | 0.2632 | 379.53 | 15.61 | 17.21 | 1.34 |
| 0.6599 | 0.2357 | 381.63 | 14.21 | 15.91 | 1.33 |
| 0.6789 | 0.2120 | 382.87 | 13.91 | 14.76 | 1.41 |
| 0.6979 | 0.1883 | 383.94 | 13.43 | 13.43 | 1.50 |
| 0.7169 | 0.1647 | 384.70 | 12.63 | 11.92 | 1.59 |
| 0.7428 | 0.1424 | 386.19 | 10.75 | 10.25 | 1.56 |
| 0.7730 | 0.1203 | 388.42 | 8.57 | 8.48 | 1.48 |
| $T/K = 308.15$ | | | | | |
| 0.0959 | 0.7916 | 317.18 | 12.37 | 13.15 | 2.24 |
| 0.1161 | 0.7751 | 321.84 | 14.27 | 15.01 | 2.14 |
| 0.1576 | 0.7413 | 330.37 | 17.12 | 17.58 | 1.93 |
| 0.1780 | 0.7204 | 334.03 | 18.53 | 18.53 | 1.89 |
| 0.1986 | 0.6994 | 337.36 | 19.56 | 19.40 | 1.85 |
| 0.2194 | 0.6781 | 340.69 | 20.59 | 20.19 | 1.81 |
| 0.2404 | 0.6567 | 343.67 | 21.24 | 20.89 | 1.77 |
| 0.2603 | 0.6320 | 346.55 | 22.45 | 21.70 | 1.81 |
| 0.2801 | 0.6073 | 349.21 | 23.48 | 22.41 | 1.85 |
| 0.2999 | 0.5827 | 351.80 | 24.42 | 23.01 | 1.89 |
| 0.3197 | 0.5581 | 354.18 | 25.16 | 23.50 | 1.93 |
| 0.3429 | 0.5387 | 357.00 | 24.86 | 23.57 | 1.83 |
| 0.3664 | 0.5191 | 359.42 | 24.12 | 23.55 | 1.74 |
| 0.3904 | 0.4990 | 361.97 | 23.46 | 23.46 | 1.64 |
| 0.4149 | 0.4786 | 364.32 | 22.50 | 23.26 | 1.55 |

**Table 3** continued

| $x_1$ | $x_2$ | $(C_P)_{123}$/J $K^{-1}$ $mol^{-1}$ | $(C_P^E)_{123}$/J $K^{-1}$ $mol^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Exptl. | Graph | Flory |
| 0.4398 | 0.4577 | 366.47 | 21.32 | 22.98 | 1.46 |
| 0.4628 | 0.4343 | 368.66 | 20.94 | 22.73 | 1.44 |
| 0.5030 | 0.3945 | 372.30 | 19.96 | 21.03 | 1.41 |
| 0.5171 | 0.3767 | 373.69 | 20.22 | 21.75 | 1.46 |
| 0.5307 | 0.3594 | 375.10 | 20.55 | 21.42 | 1.52 |
| 0.5441 | 0.3426 | 376.33 | 20.68 | 21.05 | 1.57 |
| 0.5571 | 0.3261 | 377.46 | 20.77 | 20.63 | 1.62 |
| 0.5697 | 0.3101 | 378.50 | 20.80 | 20.17 | 1.67 |
| 0.5948 | 0.2889 | 380.23 | 19.19 | 19.19 | 1.61 |
| 0.6128 | 0.2760 | 381.59 | 17.87 | 18.47 | 1.53 |
| 0.6307 | 0.2632 | 382.76 | 16.36 | 17.73 | 1.46 |
| 0.6599 | 0.2357 | 384.80 | 14.87 | 15.34 | 1.44 |
| 0.6789 | 0.2120 | 386.04 | 14.53 | 15.19 | 1.53 |
| 0.6979 | 0.1883 | 386.97 | 13.90 | 13.90 | 1.62 |
| 0.7169 | 0.1647 | 387.62 | 12.97 | 12.45 | 1.71 |
| 0.7428 | 0.1424 | 389.16 | 11.11 | 10.80 | 1.68 |
| 0.7730 | 0.1203 | 391.42 | 8.92 | 9.02 | 1.59 |

Standard uncertainties, $u$, are $u(C_P)_{123} = \pm 0.8\%$; $u\ (C_P^E)_{123} = \pm 1.1\%$; $u\ (T)$ (DSC) = ±0.02 K

$$\sigma(C_P^E)_{123} = \left\{ \left[ \sum (C_P^E)_{123} - (C_P^E)_{123\{calc.\mathrm{Eq.}(2)\}} \right]^2 / (m-n) \right\}^{0.5} \quad (3)$$

where $m$ is the number of data points and $n$ is the number of ternary adjustable parameters of Eq. (2), which are presented in Table 4. It was found that Redlich–Kister equation represents satisfactorily the experimental $(C_P^E)_{123}$ for the examined mixtures. The various surfaces generated by $(C_P^E)_{123}$ values of the studied mixtures at 298.15 K are shown in Figs. 1–4.

## Discussion

The measured $(C_P)_{123}$ data for [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] or [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures at (293.15, 298.15, 303.15 and 308.15) K are not available in the literature with which the observed data can be compared. The $(C_P^E)_{123}$ data of [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) are positive over entire composition range of (1) and (2) components of the mixtures. However, the sign as well as magnitude of $(C_P^E)_{123}$ values for [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures are dictated by the relative proportion of the constituents. The $(C_P^E)_{123}$ data of mixture indicate the variation of mixture entropy with that of ideal system [46]. The $(C_P^E)_{123}$ data of [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) suggest the contribution to $(C_P^E)_{123}$ due to the formation of 1:2:3 molecular complex (possessing non-random structure) in mixed state far outweighs the contribution due to the destruction of molecular entities of [Bmmim][$BF_4$] or [Emim][$BF_4$] or cyclopentanone or cyclohexanone which in turn enhance randomness and increase in entropy of the mixture. Further, $(C_P^E)_{123}$ values of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclohexanone (3) mixture are higher than those of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone (3) mixture which in turn indicate strong interactions between the cyclohexanone and [Bmmim][$BF_4$]: [Bmim][$BF_4$] molecular entity as compared to cyclopentanone. This may be due to reason that cyclohexanone is more basic in nature and possess chair form [47] and thus can interact strongly and packed efficiently with [Bmmim][$BF_4$]: [Bmim][$BF_4$] molecular entity [11].

The $(C_P^E)_{123}$ values of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] or [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures suggest strong interactions between cyclopentanone or cyclohexanone and [Bmmim][$BF_4$]: [Emim][$BF_4$] as compared to [Bmmim][$BF_4$]: [Bmim][$BF_4$] molecular entity. It may be due to the presence of bulky $-CH_3$ group in [Bmim][$BF_4$] which in turn restricts the approach of cyclopentanone or cyclohexanone toward [Bmmim][$BF_4$]: [Bmim][$BF_4$] molecular entity. The $\partial(C_P^E)_{123}/\partial T$ for the studied ternary mixtures is positive indicating the rupture of interactions among molecular entities [Bmmim][$BF_4$] or [Bmim][$BF_4$] or [Emim][$BF_4$] or cyclopentanone or cyclohexanone is more difficult in pure state as compared to mixed state [48].

## Graph theory

The Moelwyn–Huggins concept [49, 50] of interaction between the surfaces of components of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] or [Emim][$BF_4$] (2); [Bmmim][$BF_4$] or [Bmim][$BF_4$] (1) + cyclopentanone or cyclohexanone (2) binary mixtures has been successfully utilized (taking into consideration the topology of the components of the mixture) to determine excess molar volumes, $V^E$, excess isentropic compressibilities, $(\kappa_S^E)$, excess heat capacities, $C_P^E$, and excess molar enthalpies, $H^E$ of (1 + 2) mixtures. The analyses of $V^E$, $(\kappa_S^E)$, $C_P^E$ and $H^E$ data in terms of Moelwyn–Huggins concept (Graph theory), IR and quantum mechanical studies have revealed that ILs: [Bmmim][$BF_4$], [Bmim][$BF_4$] and [Emim][$BF_4$] exist as

**Table 4** Ternary adjustable parameters, $(C_P)_{123}^{(n)}$ ($n$ = 0–2) parameters along with the standard deviations, $\sigma(C_P^E)_{123}$, at $T$ = (293.15–308.15) K

| Parameters | *T*/K | | | |
|---|---|---|---|---|
| | 293.15 | 298.15 | 303.15 | 308.15 |
| [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone (3) | | | | |
| $C_p^{(0)}$/J $K^{-1}$ $mol^{-1}$ | 51.29 | 57.94 | 62.06 | 67.69 |
| $C_p^{(1)}$/J $K^{-1}$ $mol^{-1}$ | −4957.51 | −4201.33 | −3524.14 | −2804.84 |
| $C_p^{(2)}$/J $K^{-1}$ $mol^{-1}$ | −76,033.44 | −76,466.46 | −76,348.92 | −76,631.42 |
| $\sigma(C_p^E)_{123}$/J $K^{-1}$ $mol^{-1}$ | 0.05 | 0.05 | 0.04 | 0.04 |
| [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclohexanone (3) | | | | |
| $C_p^{(0)}$/J $K^{-1}$ $mol^{-1}$ | 69.88 | 99.50 | 144.83 | 186.65 |
| $C_p^{(1)}$/J $K^{-1}$ $mol^{-1}$ | −4093.56 | −3881.24 | −3621.66 | −3404.42 |
| $C_p^{(2)}$/J $K^{-1}$ $mol^{-1}$ | −73,658.90 | −71,067.16 | −67,477.10 | −64,550.59 |
| $\sigma(C_p^E)_{123}$/J $K^{-1}$ $mol^{-1}$ | 0.04 | 0.04 | 0.04 | 0.04 |
| [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone (3) | | | | |
| $C_p^{(0)}$/J $K^{-1}$ $mol^{-1}$ | 1101.64 | 1090.22 | 1080.66 | 1069.62 |
| $C_p^{(1)}$/J $K^{-1}$ $mol^{-1}$ | 3283.18 | 3387.79 | 3502.49 | 3880.62 |
| $C_p^{(2)}$/J $K^{-1}$ $mol^{-1}$ | −9193.28 | −6077.61 | −5629.29 | −3450.75 |
| $\sigma(C_p^E)_{123}$/J $K^{-1}$ $mol^{-1}$ | 0.07 | 0.07 | 0.07 | 0.08 |
| [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclohexanone (3) | | | | |
| $C_p^{(0)}$/J $K^{-1}$ $mol^{-1}$ | 1081.34 | 1099.14 | 1127.77 | 1135.38 |
| $C_p^{(1)}$/J $K^{-1}$ $mol^{-1}$ | 1166.69 | 1030.55 | 816.01 | 617.81 |
| $C_p^{(2)}$/J $K^{-1}$ $mol^{-1}$ | −14,572.93 | −12,089.50 | −10,528.08 | −8337.23 |
| $\sigma(C_p^E)_{123}$/J $K^{-1}$ $mol^{-1}$ | 0.04 | 0.04 | 0.05 | 0.05 |

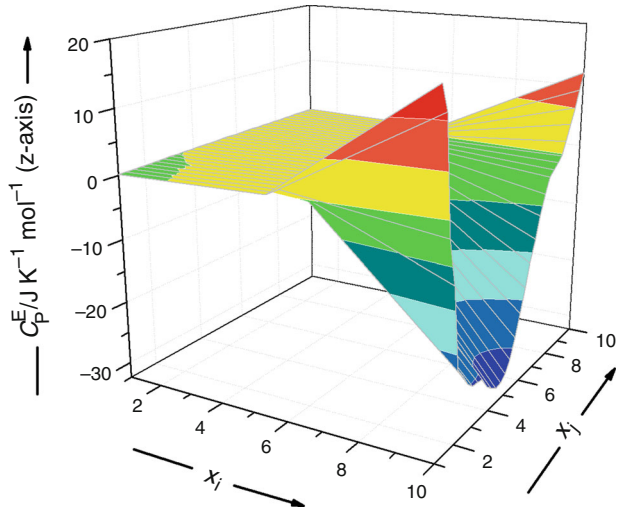


**Fig. 1** Surface generated for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-butyl-3-methylimidazolium tetrafluoroborate (2) + cyclopentanone (3) by excess heat capacities $\left(C_P^E\right)_{123}$ data at 298.15 K

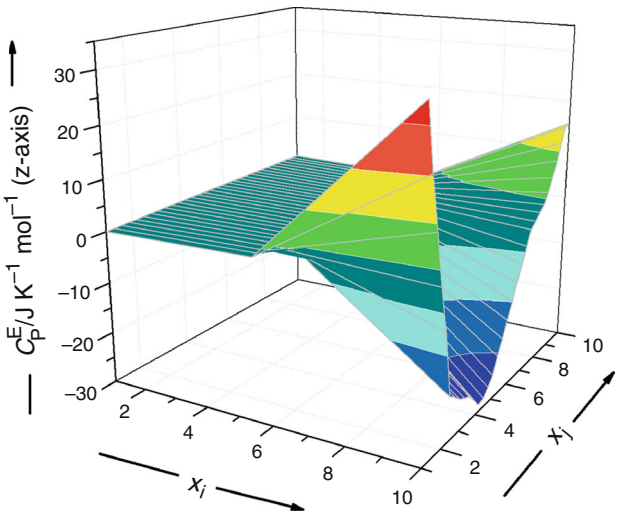


**Fig. 2** Surface generated for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-butyl-3-methylimidazolium tetrafluoroborate (2) + cyclohexanone (3) by excess heat capacities $\left(C_P^E\right)_{123}$ data at 298.15 K

monomer (characterized by cohesion forces; H-bonding occurs between hydrogen atom/s of methyl group/s attached to imidazolium ring with fluorine atoms of $BF_4$ [11]); cyclopentanone, cyclohexanone are characterized by dipole–dipole interactions as well as Debye and London forces and exist as associated molecular entities.

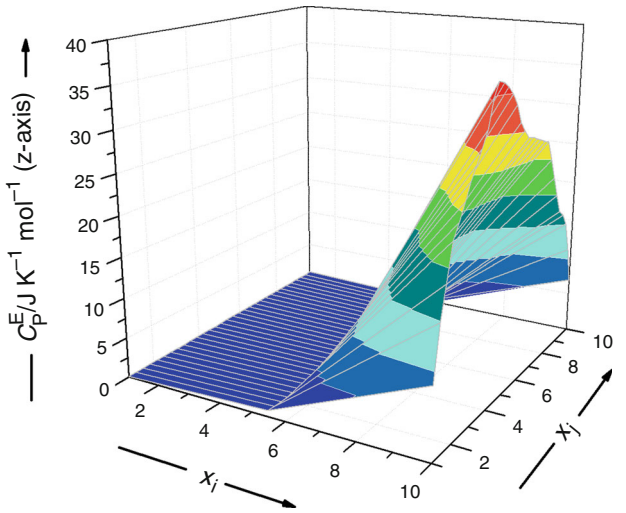


**Fig. 3** Surface generated for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-ethyl-3-methylimidazolium tetrafluoroborate (2) + cyclopentanone (3) by excess heat capacities $\left(C_P^E\right)_{123}$ data at 298.15 K

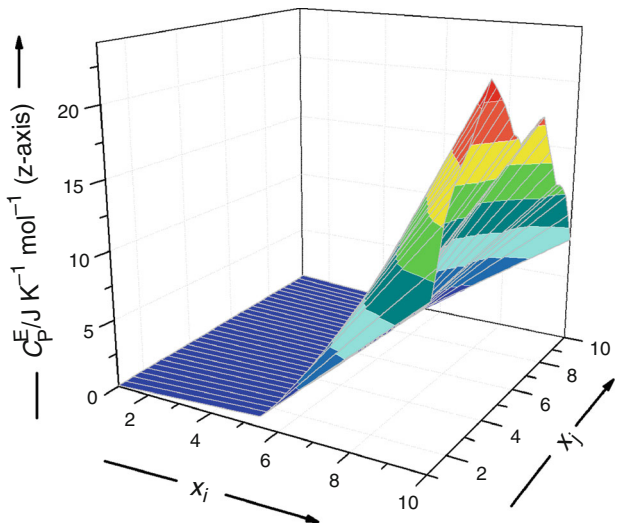


**Fig. 4** Surface generated for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + 1-ethyl-3-methylimidazolium tetrafluoroborate (2) + cyclohexanone (3) by excess heat capacities $\left(C_P^E\right)_{123}$ data at 298.15 K

The addition of third component like cyclopentanone or cyclohexanone to molecular entities [Bmmim][$BF_4$]: [Bmim][$BF_4$] and [Bmmim][$BF_4$]: [Emim][$BF_4$] results in the formation of ternary [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) and [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures. The various processes involved in (1 + 2 + 3) mixtures formation may be assumed to be comprised of the processes: (I) establishment of unlike (a) 1–2, (b) 2–$3_n$ ($n = 2$), (c) 1–$3_n$ contacts; (II) unlike contact formation then leads to rupture of (a) cohesion forces in [Bmmim][$BF_4$] or [Bmim][$BF_4$] or [Emim][$BF_4$]; and (b) dipole–dipole interactions in cyclopentanone or cyclohexanone which in turn yields their respective monomers; and (III) molecules of 1, 2 and 3 then undergo interactions to form (a) 1:2 (b) 2:3 and (c) 1:3 molecular complexes.

If $\chi_{12}$, $\chi_{23}$, $\chi_{13}$ are molar interaction parameters for (I) unlike 1–2; 2–$3_n$; 1–$3_n$ contacts (leading to enhancement of non-randomness); then change in thermodynamic property, $\Delta C_P$, due to processes I (a)–(c) was expressed by [51–53].

$$(\Delta C_P)_I = \left[\frac{x_1 x_2 ({}^3\xi_1/{}^3\xi_2)\chi_{12}}{x_1 + x_2({}^3\xi_1/{}^3\xi_2)}\right] + \left[\frac{x_2 x_3 ({}^3\xi_2/{}^3\xi_3)\chi_{23}}{x_2 + x_3({}^3\xi_2/{}^3\xi_3)}\right] + \left[\frac{x_3 x_1 ({}^3\xi_3/{}^3\xi_1)\chi_{13}}{x_3 + x_1({}^3\xi_3/{}^3\xi_1)}\right] \quad (4)$$

Further, if $\chi_{11}$, $\chi_{22}$, $\chi_{33}$; and $\chi_{12}'$, $\chi_{12}''$ $\chi_{12}'''$ are molar interaction parameters for rupture of cohesion forces in ILs and dipole–dipole interactions in cyclopentanone and cyclohexanone (increase in randomness) and specific interactions between 1, 2 and 3 molecules to form 1:2, 2:3, 1:3 molecular complexes (possessing non-random structure), respectively, and then change in $\Delta C_P$ due to processes II (a)–(b); and III (a)–(c) was given by [54, 55].

$$(\Delta C_P)_{II} = \left[\frac{x_1^2 x_2 ({}^3\xi_1/{}^3\xi_2)\chi_{11}}{x_1 + x_2({}^3\xi_1/{}^3\xi_2)}\right] + \left[\frac{x_2^2 x_3 ({}^3\xi_2/{}^3\xi_3)\chi_{22}}{x_2 + x_3({}^3\xi_2/{}^3\xi_3)}\right] + \left[\frac{x_3^2 x_1 ({}^3\xi_3/{}^3\xi_1)\chi_{33}}{x_3 + x_1({}^3\xi_3/{}^3\xi_1)}\right] \quad (5)$$

$$(\Delta C_P)_{III} = \left[\frac{x_1 x_2^2 ({}^3\xi_1/{}^3\xi_2)\chi_{12}'}{x_1 + x_2({}^3\xi_1/{}^3\xi_2)}\right] + \left[\frac{x_2 x_3^2 ({}^3\xi_2/{}^3\xi_3)\chi_{12}''}{x_2 + x_3({}^3\xi_2/{}^3\xi_3)}\right] + \left[\frac{x_3 x_1^2 ({}^3\xi_3/{}^3\xi_1)\chi_{12}'''}{x_3 + x_1({}^3\xi_3/{}^3\xi_1)}\right] \quad (6)$$

The total change in thermodynamic properties due to processes: I (a)–(c); II (a)–(b); and III (a)–(c) was presented by

$$\begin{aligned}\left(C_P^E\right)_{123} &= \sum_{i=I}^{III} (\Delta C_{Pi}) \\ &= \left[\frac{x_1 x_2 ({}^3\xi_1/{}^3\xi_2)}{x_1 + x_2({}^3\xi_1/{}^3\xi_2)}\right]\left[\chi_{12} + x_1\chi_{11} + x_2\chi_{12}'\right] \\ &+ \left[\frac{x_2 x_3 ({}^3\xi_2/{}^3\xi_3)}{x_2 + x_3({}^3\xi_2/{}^3\xi_3)}\right]\left[\chi_{23} + x_2\chi_{22} + x_3\chi_{12}''\right] \\ &+ \left[\frac{x_3 x_1 ({}^3\xi_3/{}^3\xi_1)}{x_3 + x_1({}^3\xi_3/{}^3\xi_1)}\right]\left[\chi_{13} + x_3\chi_{33} + x_1\chi_{12}'''\right]\end{aligned} \quad (7)$$

For the present mixtures, it was assumed that (i) interaction parameters for the establishment of unlike contacts 1–2; 2–$3_n$; 1–$3_n$ are nearly equal to the interaction parameters for the formation of 1:2, 2:3, 1:3 molecular complexes; and (ii) interaction parameters for the rupture

of cohesion forces in (1) or (2) or (3) components are nearly equal then, $\chi_{12} \cong \chi'_{12} = \chi^*_{12}$; $\chi_{23} \cong \chi''_{12} = -\chi^*_{23}$;$\chi_{13} \cong \chi'''_{12} = \chi^*_{13}$; $\chi_{11} \cong \chi_{22} \cong \chi_{33} = \chi^*$, Eq. (7) was then expressed as

$$(C_P^E)_{123} = \left[\frac{x_1 x_2 ({}^3\xi_1/{}^3\xi_2)}{x_1 + x_2({}^3\xi_1/{}^3\xi_2)}\right]\left[(1+x_2)\chi^*_{12} + x_1\chi^*\right] + \left[\frac{x_2 x_3 ({}^3\xi_2/{}^3\xi_3)}{x_2 + x_3({}^3\xi_2/{}^3\xi_3)}\right]\left[(1+x_3)\chi^*_{23} + x_2\chi^*\right] + \left[\frac{x_3 x_1 ({}^3\xi_3/{}^3\xi_1)}{x_3 + x_1({}^3\xi_3/{}^3\xi_1)}\right]\left[(1+x_1)\chi^*_{13} + x_3\chi^*\right] \quad (8)$$

Equation (8) contains four unknown parameters: $\chi^*_{12}$, $\chi^*_{23}$, $\chi^*_{31}$ and $\chi^*$ and these parameters were evaluated by utilizing $(C_P^E)_{123}$ data of the examined mixtures at four arbitrary compositions. The calculated parameters were then used to predict $(C_P^E)_{123}$ values at various values of $x_1$ and $x_2$. Such obtained $(C_P^E)_{123}$ values for the investigated mixtures are presented in Table 3 and also compared with their experimental values. The molar interaction parameters: $\chi^*_{12}$, $\chi^*_{23}$, $\chi^*_{31}$ and $\chi^*$evaluated by utilizing $(C_P^E)_{123}$ data for the various mixtures are listed in Table 5. The standard deviations between experimental and calculated values (by Graph theory), $\sigma\,(C_P^E)_{123}$, are also recorded in Table 5. An examination of Table 3 has revealed that $(C_P^E)_{123}$ values determined by Graph theory compare well their corresponding experimental values which in turn support the various assumptions made in deriving Eq. (8).

## Flory's theory

Flory's theory was used to correlate the $(C_P^E)_{123}$ results for the present mixtures which in turn were obtained by differentiating excess molar enthalpies of ternary mixtures with respect to the temperature, $T$ [48, 56, 57]. The theory leads to the following expression for $(C_P^E)_{123}$

$$(C_P^E)_{123} = -\sum_{1=1}^{3}\frac{x_1 P_1^* \tilde{v}_1^* \alpha_1}{\tilde{v}_1} + \left(\frac{\alpha}{\tilde{v}}\right)\left[\sum_{1=1}^{3} x_1 P_1^* v_1^* - \sum_{1=1}^{3} x_1 v_1^* \theta_2 \chi_{12}^{**}\right] \quad (9)$$

where $\tilde{v}_1^*$, $P_1^*$, $\alpha_1$, $\tilde{v}_1$ and $\theta_2(1 = 1$ or 2 or 3) are the characteristic volume, characteristic pressure, thermal coefficient, reduced volume and molecular surface fraction of pure component (1) or (2) or (3) and $\tilde{v}$, $\alpha$ and $\chi_{12}^{**}$ are reduced volume, thermal coefficient and interactional energy parameter of mixture and have the same significance as described elsewhere [56]. The values of such parameters for pure liquids are also listed in Table 6. The estimation of $(C_P^E)_{123}$ data by Flory theory requires a knowledge of Flory parameters for liquids under investigation along with interaction parameters of (1 + 2), (2 + 3), (1 + 3) binaries which in turn were evaluated by utilizing their $H^E$ values at equimolar composition using equation:

$$H^E = \sum x_1 P_1^* (\widetilde{U}_1^{-1} - \widetilde{U}_{cal}^{-1}) + x_1 v_1^* \theta_2 \chi_{12}^{**} \widetilde{U}_{cal}^{-1} \quad (10)$$

where $x_1$, $P_1^*$, $v_1^*$, $\theta_2$, $\chi_{12}^{**}$, $\widetilde{U}_1$, and $\widetilde{U}_{cal}$ are mole fraction, characteristic pressure, characteristic volume, molecular surface fraction of pure component (1) or (2) or (3), interactional energy parameter of mixture, reduced configurational energy and calculated reduced configurational energy and have the same significance as described elsewhere [58]. Such calculated Flory parameters are listed in Table 6. Benson and D' Arcy [59] further suggested that interaction parameters, $\chi_{12}^{**}$, $\chi_{23}^{**}$, $\chi_{13}^{**}$ for (1 + 2), (2 + 3), (1 + 3) binary mixtures must be a function of temperature.

Consequently, $(C_P^E)_{123}$ values were then expressed by

$$(C_P^E)_{123} = -\sum_{1=1}^{3}\frac{x_1 P_1^* \tilde{v}_1^* \alpha_1}{\tilde{v}_1} + \left(\frac{\alpha}{\tilde{v}}\right)\left[\sum_{1=1}^{3} x_1 P_1^* v_1^* - \sum_{1=1}^{3} x_1 v_1^* \theta_2 \chi_{12}^{**}\right] + \sum_{1=1}^{3}\frac{x_1 v_1^* \theta_2}{\tilde{v}}\left(\frac{\partial \chi_{12}^{**}}{\partial T}\right) \quad (11)$$

The reduced volumes, $\tilde{v}$, and thermal coefficient, $\alpha$, of ternary mixtures were calculated using

$$\tilde{v} = \left(V_{123}^E + \sum_{1=1}^{3} x_1 v_1\right) \Big/ \sum_{1=1}^{3} x_1 v_1^* \quad (12)$$

$$\alpha = \sum_{1=1}^{3} x_1 \alpha_1 \quad (13)$$

where $V_{123}^E$ represent excess molar volumes of ternary (1 + 2 + 3) mixtures. The calculated $(C_P^E)_{123}$ values are presented and compared with experimental values in Table 3. Examination of data in Table 3 has revealed that Flory's theory correctly predicts the sign of $(C_P^E)_{123}$ values of [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures. However, quantitative agreement is poor. The failure of theory to correctly predict the sign of $(C_P^E)_{123}$ data of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures may be due to strong interactions operating among the various components.

**Table 5** Interaction energies: $\chi^{*}_{12}$,$\chi^{*}_{23}$, $\chi^{*}_{31}$ and $\chi^{*}$ parameters of Eq. (8) and $\chi^{**}_{12}$, $\chi^{**}_{23}$, $\chi^{**}_{13}$ parameters of Flory theory along with connectivity parameters of third degree of a molecule, $({}^{3}\xi_1)$ or $({}^{3}\xi_1)_{\mathrm{m}}$ (1 = 1 or 2 or 3) utilized in Graph theory for the determination of $\left(C^{\mathrm{E}}_{\mathrm{P}}\right)_{123}$ at $T$ = (293.15–308.15) K

| Parameters | *T/K* | | | |
|---|---|---|---|---|
| | 293.15 | 298.15 | 303.15 | 308.15 |
| [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone (3) | | | | |
| $({}^{3}\xi_1) = ({}^{3}\xi_1)_{\mathrm{m}}$ | 3.403 | 3.403 | 3.403 | 3.403 |
| $({}^{3}\xi_2) = ({}^{3}\xi_2)_{\mathrm{m}}$ | 2.396 | 2.396 | 2.396 | 2.396 |
| $({}^{3}\xi_3) = ({}^{3}\xi_3)_{\mathrm{m}}$ | 1.287 | 1.287 | 1.287 | 1.287 |
| $\chi^{*}_{12}$/J K$^{-1}$ mol$^{-1}$ | −294.16 | −290.48 | −288.64 | −283.89 |
| $\chi^{*}_{23}$/J K$^{-1}$ mol$^{-1}$ | −36.82 | −37.49 | −39.00 | −41.51 |
| $\chi^{*}_{13}$/J K$^{-1}$ mol$^{-1}$ | 54.47 | 37.65 | 21.71 | 8.55 |
| $\chi^{*}$/J K$^{-1}$ mol$^{-1}$ | 420.80 | 432.15 | 446.81 | 456.32 |
| $\sigma(C^{\mathrm{E}}_{\mathrm{p}})_{123}$/J K$^{-1}$ mol$^{-1}$(Graph) | 1.52 | 1.53 | 1.40 | 1.35 |
| $\chi^{**}_{12}$/J cm$^{-3}$ | 0.90 | 0.72 | 0.58 | 0.55 |
| $\chi^{**}_{23}$/J cm$^{-3}$ | −0.10 | −0.01 | 0.14 | 0.18 |
| $\chi^{**}_{13}$/J cm$^{-3}$ | 1.78 | 1.72 | 1.73 | 1.73 |
| $\sigma(C^{\mathrm{E}}_{\mathrm{p}})_{123}$/J K$^{-1}$ mol$^{-1}$(Flory) | 19.63 | 19.17 | 18.67 | 17.73 |
| [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclohexanone (3) | | | | |
| $({}^{3}\xi_1) = ({}^{3}\xi_1)_{\mathrm{m}}$ | 3.403 | 3.403 | 3.403 | 3.403 |
| $({}^{3}\xi_2) = ({}^{3}\xi_2)_{\mathrm{m}}$ | 2.396 | 2.396 | 2.396 | 2.396 |
| $({}^{3}\xi_3) = ({}^{3}\xi_3)_{\mathrm{m}}$ | 2.105 | 2.105 | 2.105 | 2.105 |
| $\chi^{*}_{12}$/J K$^{-1}$ mol$^{-1}$ | −325.42 | −313.10 | −298.74 | −286.11 |
| $\chi^{*}_{23}$/J K$^{-1}$ mol$^{-1}$ | 248.97 | 243.83 | 234.33 | 229.39 |
| $\chi^{*}_{13}$/J K$^{-1}$ mol$^{-1}$ | −14.35 | −19.90 | −27.02 | −28.08 |
| $\chi^{*}$/J K$^{-1}$ mol$^{-1}$ | 396.59 | 385.68 | 378.74 | 366.30 |
| $\sigma(C^{\mathrm{E}}_{\mathrm{p}})_{123}$/J K$^{-1}$ mol$^{-1}$(Graph) | 1.22 | 1.08 | 1.18 | 1.35 |
| $\chi^{**}_{12}$/J cm$^{-3}$ | 0.90 | 0.72 | 0.58 | 0.55 |
| $\chi^{**}_{23}$/J cm$^{-3}$ | 0.45 | 0.58 | 0.79 | 0.87 |
| $\chi^{**}_{13}$/J cm$^{-3}$ | 1.75 | 1.81 | 1.99 | 2.06 |
| $\sigma(C^{\mathrm{E}}_{\mathrm{p}})_{123}$/J K$^{-1}$ mol$^{-1}$(Flory) | 18.72 | 18.23 | 17.43 | 16.42 |
| [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone (3) | | | | |
| $({}^{3}\xi_1) = ({}^{3}\xi_1)_{\mathrm{m}}$ | 3.403 | 3.403 | 3.403 | 3.403 |
| $({}^{3}\xi_2) = ({}^{3}\xi_2)_{\mathrm{m}}$ | 1.639 | 1.639 | 1.639 | 1.639 |
| $({}^{3}\xi_3) = ({}^{3}\xi_3)_{\mathrm{m}}$ | 1.287 | 1.287 | 1.287 | 1.287 |
| $\chi^{*}_{12}$/J K$^{-1}$ mol$^{-1}$ | 128.97 | 143.02 | 139.75 | 147.22 |
| $\chi^{*}_{23}$/J K$^{-1}$ mol$^{-1}$ | 50.44 | 53.84 | 58.25 | 73.60 |
| $\chi^{*}_{13}$/J K$^{-1}$ mol$^{-1}$ | −22.95 | 3.72 | 7.81 | 75.18 |
| $\chi^{*}$/J K$^{-1}$ mol$^{-1}$ | −142.38 | −178.23 | −169.62 | −219.02 |
| $\sigma(C^{\mathrm{E}}_{\mathrm{p}})_{123}$/J K$^{-1}$ mol$^{-1}$(Graph) | 1.64 | 1.58 | 1.54 | 1.52 |
| $\chi^{**}_{12}$/J cm$^{-3}$ | 0.99 | 0.90 | 0.93 | 0.93 |
| $\chi^{**}_{23}$/J cm$^{-3}$ | 10.23 | 10.71 | 10.51 | 10.33 |
| $\chi^{**}_{13}$/J cm$^{-3}$ | 1.78 | 1.72 | 1.73 | 1.73 |
| $\sigma(C^{\mathrm{E}}_{\mathrm{p}})_{123}$/J K$^{-1}$ mol$^{-1}$(Flory) | 25.65 | 26.94 | 28.22 | 31.01 |
| [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclohexanone (3) | | | | |
| $({}^{3}\xi_1) = ({}^{3}\xi_1)_{\mathrm{m}}$ | 3.403 | 3.403 | 3.403 | 3.403 |
| $({}^{3}\xi_2) = ({}^{3}\xi_2)_{\mathrm{m}}$ | 1.639 | 1.639 | 1.639 | 1.639 |
| $({}^{3}\xi_3) = ({}^{3}\xi_3)_{\mathrm{m}}$ | 2.105 | 2.105 | 2.105 | 2.105 |

**Table 5** continued

| Parameters | *T/K* | | | |
|---|---|---|---|---|
| | 293.15 | 298.15 | 303.15 | 308.15 |
| $\chi^{*}_{12}$/J K$^{-1}$ mol$^{-1}$ | 28.91 | 34.94 | 38.94 | 46.21 |
| $\chi^{*}_{23}$/J K$^{-1}$ mol$^{-1}$ | 114.06 | 118.12 | 121.23 | 115.53 |
| $\chi^{*}_{13}$/J K$^{-1}$ mol$^{-1}$ | −43.18 | −43.22 | −40.37 | −27.11 |
| $\chi^{*}$/J K$^{-1}$ mol$^{-1}$ | 10.22 | 4.18 | −0.64 | −17.64 |
| $\sigma(C^{E}_{p})_{123}$/J K$^{-1}$ mol$^{-1}$(Graph) | 1.23 | 1.20 | 1.13 | 0.94 |
| $\chi^{**}_{12}$/J cm$^{-3}$ | 0.99 | 0.90 | 0.93 | 0.93 |
| $\chi^{**}_{23}$/J cm$^{-3}$ | 4.53 | 4.98 | 5.44 | 5.20 |
| $\chi^{**}_{13}$/J cm$^{-3}$ | 1.75 | 1.81 | 1.99 | 2.06 |
| $\sigma(C^{E}_{p})_{123}$/J K$^{-1}$ mol$^{-1}$(Flory) | 15.56 | 16.65 | 18.12 | 18.74 |

Also included are the deviations, $\sigma\left(C^{E}_{P}\right)_{123}$, between experimental and calculated $\left(C^{E}_{P}\right)_{123}$ values by investigated theories

**Table 6** Parameters of pure components, Characteristic volume, *V**, characteristic pressure, *P**, molar volume, *V*, reduced volume, $\tilde{v}$ and thermal expansion coefficient, $\alpha$, used in Flory theory calculations at $T = (293.15–308.15)$ K

| Components | *T/*K | *V**/cm$^3$ mol$^{-1}$ | *P**/J cm$^{-3}$ | *V*/cm$^3$ mol$^{-1}$ | $\tilde{v}$ /cm$^3$ mol$^{-1}$ | $\alpha$ ($\times 10^{-3}$)/K$^{-1}$ |
|---|---|---|---|---|---|---|
| *1-butyl-2,3-dimethyl imidazolium tetrafluoroborate* | 293.15 | 185.73 | 324.67 | 201.13 | 1.08 | 0.299 |
| | 298.15 | 184.76 | 351.26 | 201.42 | 1.09 | 0.322 |
| | 303.15 | 184.51 | 360.43 | 201.78 | 1.09 | 0.329 |
| | 308.15 | 184.23 | 369.48 | 202.08 | 1.10 | 0.336 |
| *1-butyl-3-methyl imidazolium tetrafluoroborate* | 293.15 | 159.60 | 687.93 | 187.86 | 1.18 | 0.687 |
| | 298.15 | 160.95 | 656.03 | 188.52 | 1.17 | 0.650 |
| | 303.15 | 162.68 | 611.45 | 189.08 | 1.16 | 0.601 |
| | 308.15 | 163.11 | 605.63 | 189.66 | 1.16 | 0.594 |
| *1-ethyl-3-methyl imidazolium tetrafluoroborate* | 293.15 | 132.84 | 689.00 | 153.98 | 1.16 | 0.609 |
| | 298.15 | 133.31 | 678.42 | 154.46 | 1.16 | 0.596 |
| | 303.15 | 132.93 | 700.33 | 154.91 | 1.17 | 0.614 |
| | 308.15 | 132.87 | 711.48 | 155.42 | 1.17 | 0.622 |
| *Cyclopentanone* | 293.15 | 71.03 | 660.42 | 88.61 | 1.25 | 1.016 |
| | 298.15 | 71.12 | 659.21 | 89.06 | 1.25 | 1.022 |
| | 303.15 | 71.20 | 658.06 | 89.52 | 1.26 | 1.030 |
| | 308.15 | 71.32 | 655.39 | 89.98 | 1.26 | 1.034 |
| *Cyclohexanone* | 293.15 | 83.90 | 633.81 | 103.59 | 1.23 | 0.953 |
| | 298.15 | 83.59 | 652.20 | 104.08 | 1.25 | 0.987 |
| | 303.15 | 83.13 | 675.54 | 104.62 | 1.26 | 1.036 |
| | 308.15 | 83.05 | 682.33 | 105.17 | 1.27 | 1.056 |

## Conclusions

Excess heat capacities, $\left(C^{E}_{P}\right)_{123}$, of ternary ionic liquid mixtures of [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] or [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) have been determined by utilizing the measured molar heat capacities $(C_P)_{123}$ data of the said mixtures at the studied temperatures. While $\left(C^{E}_{P}\right)_{123}$ values of [Bmmim][$BF_4$] (1) + [Emim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures are positive over the entire mole fraction of components (1) and (2), those for [Bmmim][$BF_4$] (1) + [Bmim][$BF_4$] (2) + cyclopentanone or cyclohexanone (3) mixtures change sign with change in relative proportion of constituent molecules. The analysis of $\left(C^{E}_{P}\right)_{123}$ data suggests that cyclohexanone gives relatively more compact structure in [Bmmim][$BF_4$]: [Bmim][$BF_4$] and [Bmmim][$BF_4$]: [Emim][$BF_4$] molecular entities as compared to cyclopentanone. The $\left(C^{E}_{P}\right)_{123}$ data have also been analyzed in terms of (i) Graph; and (ii) Flory

theories. It has been observed that values predicted by Graph theory compare well with their experimental values. However, Flory theory shows only qualitative agreement with measured values.

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