Journal of Molecular Liquids 231 (2017) 225–237

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermodynamic properties of mixtures containing 1-butyl-2,3-dimethylimidazolium tetrafluoroborate and cyclopentanone or cyclohexanone

Heena Gupta [a], Masta Chandrasekhar [b], Tadikonda Srinivasa Krishna [c], Vinod Kumar Sharma [a,*]

[a] *Department of Chemistry, M. D. University, Rohtak, Haryana, India*
[b] *Department of Physics, Vignan Institute of Technology and Science, Hyderabad, Telangana, India*
[c] *Department of Physics, Nalanda Institute of Engineering and Technology, Sathenpali, Andhra Pradesh, India*

ARTICLE INFO

Article history:
Received 31 October 2016
Received in revised form 1 February 2017
Accepted 3 February 2017
Available online 07 February 2017

Keywords:
Excess molar volumes
Excess isentropic compressibilities
Excess molar enthalpies
Connectivity parameter of third degree of a molecule
Interaction parameters

ABSTRACT

The densities, ρ, speeds of sound, u, and molar heat capacities, C_P, of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone or cyclohexanone (2) mixtures at 293.15, 298.15,303.15 and 308.15 K and excess molar enthalpies, H^E of same mixtures at 298.15 K have been measured as a function of composition. The observed ρ, u, and C_P values are used to determine excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E and excess heat capacities, C_P^E. The analysis of V^E data in terms of Graph theory has suggested that while 1-butyl-2,3-dimethylimidazolium tetrafluoroborate exists as monomer; cyclopentanone and cyclohexanone exist as mixture of open and cyclic dimer. The analysis of inter-nuclear distances among interacting atoms (predicted by quantum mechanical calculations) also supports the presence of proposed molecular entities in pure and mixed states. It has been observed that V^E, κ_S^E, C_P^E and H^E estimated by Graph theory compare well with their experimental values.

1. Introduction

Ionic liquids (ILs) due to their unique characteristics such as purely ionic character, high thermal stability at normal temperature and pressure, designable structures have been suggested materials for the replacement of organic liquids (which are flammable and toxic). They have been regarded as benign green solvents with a wide range of potential applications such as removal of pollutants, catalysis, gas separations, fuel cells etc. [1–5]. Recently, imidazolium based ILs or their mixtures with organic liquids have been widely studied [6–11] for the possibility of their use in organic reactions, separation processes and as absorbent in acidic gas absorption processes [12–15]. The trialkyl-substituted imidazolium based ILs such as 1-butyl-2,3-dimethylimidazolium tetrafluoroborate can be used as promising material for the synthesis of various metal oxide nanostructures, electroplating, electrochemical purposes and technical as well as separation processes in industries [16,17]. The cyclic ketones have important applications in the chemical industry as intermediates or as final products, being used in the synthesis of pharmaceuticals, in agricultural and cosmetic industries [18–20]. Cyclopentanone and cyclohexanone can be used as raw material in the production of cycloalkanes, caprolactam and the monomers used for the synthesis of Nylon 6 and 66 [21,22]. The multipurpose use of ILs or their mixtures with organic solvents requires reliable data on thermodynamic properties like excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E, excess heat capacities, C_P^E and excess molar enthalpies, H^E. These properties are very important for IL containing media to optimize process parameters and scale up of chemical and separation processes. The study of IL and organic liquid mixtures is also indispensable for theoretical research. As our continual investigations on mixtures containing imidazolium based ILs, we report here densities, ρ, speeds of sound, u, molar heat capacities, C_P and excess molar enthalpies, H^E, of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone or cyclohexanone (2) mixtures.

2. Experimental

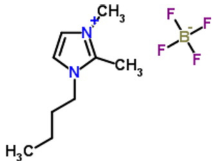
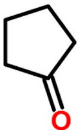
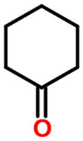
1-butyl-2,3-dimethylimidazolium tetrafluoroborate [Bmmim][BF_4] (Fluka, mass fraction: ≥0.991) was used without any further purification. The water content in [Bmmim][BF_4] was measured by Karl Fischer titration and observed to be in the range of 320–340 ppm [23]. Cyclopentanone (Fluka, mass fraction: 0.992, GC) and cyclohexanone (Fluka, mass fraction: 0.994, GC) were purified by fractional distillation [24]. The structure of studied chemicals, sources of IL/organic liquids, CAS number, purification methods and analysis methods along with their final purities are recorded in Table 1. The density and sound analyzer (Anton Paar DSA 5000) was used to measure densities, ρ, and speeds of sound, u, values of IL, purified liquids and their mixtures in

---

[*] Corresponding author.
E-mail address: v_sharmachem58@rediffmail.com (V.K. Sharma).

http://dx.doi.org/10.1016/j.molliq.2017.02.011
0167-7322/

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

Chemical name	CAS number	Source	Purification method	Initial purity	Final purity	Analysis method	Structure
1-butyl-2,3-dimethyl imidazolium tetrafluoroborate	402,846–78-0	Fluka	Used as such	≥0.991	–	–	
Cyclopentanone	120–92-3	Fluka	Fractional distillation	0.99	0.992	GC[a]	
Cyclohexanone	108-94-1	Fluka	Fractional distillation	≥0.99	0.994	GC	

[a] GC = gas chromatography.

the manner as described elsewhere [25,26]. The calibration of the apparatus for each set of the liquid mixtures was done at 293.15 K using double distilled, deionized and degassed water. The ρ and u values of IL and purified liquids are listed in Table 2 and also compared with their corresponding literature values [17,27–36]. The mole fraction in each mixture was obtained by measuring the masses of the components of mixtures using an electric balance (Mettler AX-205 Delta) with an uncertainty of $\pm 1\ 10^{-5}$ g. The standard uncertainties in the ρ and u measurements are ± 0.5 kg m^{-3} and 0.1 m s^{-1} respectively. The standard uncertainties in V^E values and temperature measurement are ±0.1% and ±0.01 K respectively.

Molar heat capacities, C_p, of pure liquids and their mixtures, excess molar enthalpies, H^E of present mixtures were measured by using a high sensitivity micro differential scanning calorimeter Micro DSC (Model–μDSC 7 Evo) supplied by M/S SETARAM instrumentation, France in the manner as described elsewhere [37,38]. The calorimeter uses a double stage temperature control with Peltier coolers and works between −45 and 120 °C. The calibration of calorimeter was done by joule effect method employing software provided by M/S SETARAM and was checked by measuring heat of fusion of naphthalene which was found to be 148.36 J g^{-1} which in turn was comparable to literature value 148.7 J g^{-1} [39]. The C_p values of IL and purified liquids along with their literature values are reported in Table 2 [28,40,41]. The standard uncertainties in measured C_p values, H^E values and temperature are ±0.3%, ±1% and ±0.02 K respectively.

The samples of (1 + 2) binary mixtures for IR studies were prepared by mixing components in 1:1 (w/w) ratio, and their IR spectra were recorded on NICOLET iS50, FT-IR spectrometer supplied by M/S Thermo Scientific, United States.

3. Results

The ρ, u and C_p data of [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) binary mixtures at 293.15, 298.15, 303.15 and

Table 2
Comparison of densities, ρ, speeds of sound, u and molar heat capacities, C_p of pure chemicals with their corresponding literature values at T = 293.15, 298.15, 303.15 and 308.15 K and atmospheric pressure 0.1 MPa.

		ρ/kg m^{-3}		u/m s^{-1}		C_p/J K^{-1} mol^{-1}	
Liquids	T/K	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
1-butyl-2,3-dimethyl imidazolium tetrafluoroborate	293.15	1193.5	1196.716 [7]	1659.7	1654.88 [7]	413.03	–
	298.15	1191.8	1191.2 [27] 1193.338 [7] 1193.19 [17]	1645.7	1641.44 [7]	416.01	–
	303.15	1189.7	1189.80 [17] 1189.921 [7]	1632.5	1628.74 [7]	418.84	–
	308.15	1187.9	1186.516 [7]	1619.8	1616.88 [7]	421.70	–
Cyclopentanone	293.15	949.3	949.34 [28]	1414.6	1414.3 [28]	152.95	152.99 [28]
	298.15	944.5	944.52 [28] 944.35 [29] 945.3 [30]	1393.6	1393.2 [28] 1394.1 [35]	154.45	154.69 [28] 154.5 [40]
	303.15	939.7	939.68 [28]	1372.6	1372.5 [28]	155.61	155.74 [28]
	308.15	934.8	934.84 [28]	1352.2	1352.6 [28]	156.76	156.81 [28]
Cyclohexanone	293.15	947.4	947.39 [28] 946.44 [31] 947.80 [32]	1431.2	1430.5 [36] 1431.9 [28]	176.17	176.19 [28]
	298.15	942.9	942.90 [28] 942.76 [33]	1414.5	1408.0 [35] 1414.8 [28]	178.27	178.37 [28] 177.97 [41]
	303.15	938.1	938.05 [28] 940.3 [34]	1395.1	1395.6 [28]	180.38	180.46 [28]
	308.15	933.2	933.18 [28] 933.80 [33]	1375.1	1375.8 [28]	182.46	182.39 [28]

Standard uncertainties, u, are u (T) (DSA) = ±0.01 K; u (ρ) = ±0.5 kg m^{-3}; u (u) = ±0.1 m s^{-1}; u (T) (DSC) = ±0.02 K; u (x_i) = $\pm 1 \cdot 10^{-4}$; u (C_p) = ±0.3%; u (P) = ±1000 Pa.

Table 3
Measured densities, ρ, excess molar volumes, V^E, speeds of sound, u, isentropic compressibilities, κ_S and excess isentropic compressibilities, κ_S^E values of the investigated mixtures as a function of mole fraction, x_1, of component (1) at $T = 293.15$, 298.15, 303.15 and 308.15 K and atmospheric pressure 0.1 MPa.

x_1	ρ_{mix} (kg m^{-3})	V^E (cm^3 mol^{-1})	u (m sec^{-1})	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)					
$T = 293.15$ K					
0.0860	970.3	2.230	1427.3	505.9	−1.36
0.1287	980.8	3.138	1434.4	495.6	−2.23
0.1731	992.0	3.922	1442.0	484.8	−3.14
0.2154	1003.1	4.499	1449.4	474.6	−3.95
0.2681	1017.7	4.960	1458.3	462.0	−4.79
0.3127	1030.5	5.154	1465.9	451.6	−5.30
0.3519	1042.2	5.160	1472.3	442.6	−5.57
0.4049	1058.7	4.924	1480.7	430.8	−5.60
0.4766	1081.7	4.235	1491.9	415.4	−5.10
0.5131	1093.5	3.753	1497.6	407.8	−4.59
0.5541	1106.8	3.112	1504.0	399.4	−3.85
0.5994	1121.2	2.336	1511.6	390.3	−2.86
0.6491	1136.5	1.431	1520.7	380.5	−1.65
0.6957	1150.1	0.577	1530.2	371.3	−0.45
0.7446	1163.0	−0.226	1541.9	361.7	0.75
0.8012	1173.9	−0.675	1559.6	350.2	1.88
0.8549	1181.3	−0.753	1580.4	338.9	2.50
0.9061	1186.9	−0.654	1604.7	327.2	2.12
$T = 298.15$ K					
0.0860	967.8	2.052	1405.3	523.2	−1.71
0.1287	979.1	2.892	1412.1	512.2	−2.68
0.1731	991.1	3.600	1419.5	500.8	−3.67
0.2154	1001.7	4.245	1427.4	490.0	−4.52
0.2681	1016.5	4.698	1436.6	476.7	−5.38
0.3127	1029.4	4.890	1444.3	465.7	−5.87
0.3519	1041.0	4.919	1451.0	456.2	−6.12
0.4049	1057.5	4.695	1459.8	443.7	−6.16
0.4766	1080.7	3.995	1471.4	427.4	−5.61
0.5131	1092.3	3.548	1477.6	419.3	−5.09
0.5541	1105.6	2.916	1484.5	410.4	−4.35
0.5994	1120.0	2.150	1492.6	400.7	−3.36
0.6491	1135.5	1.226	1502.2	390.3	−2.13
0.6957	1149.0	0.397	1512.4	380.5	−0.93
0.7446	1161.7	−0.366	1524.8	370.2	0.28
0.8012	1172.6	−0.801	1543.3	358.1	1.45
0.8549	1180.5	−0.937	1564.5	346.1	2.13
0.9061	1185.9	−0.793	1589.7	333.7	1.77
$T = 303.15$ K					
0.0860	965.1	1.884	1383.6	541.3	−2.09
0.1287	977.2	2.653	1390.1	529.6	−3.16
0.1731	989.8	3.306	1397.3	517.4	−4.22
0.2154	1000.2	3.985	1405.6	506.0	−5.09
0.2681	1015.3	4.413	1414.9	492.0	−5.96
0.3127	1028.2	4.613	1422.9	480.4	−6.48
0.3519	1040.1	4.611	1429.7	470.4	−6.70
0.4049	1056.4	4.423	1439.0	457.1	−6.70
0.4766	1079.8	3.707	1451.1	439.8	−6.14
0.5131	1091.4	3.265	1457.6	431.2	−5.61
0.5541	1104.5	2.667	1465.1	421.8	−4.84
0.5994	1118.8	1.922	1473.8	411.5	−3.83
0.6491	1134.3	1.006	1484.0	400.3	−2.60
0.6957	1147.8	0.184	1494.8	389.9	−1.39
0.7446	1160.4	−0.556	1508.0	378.9	−0.17
0.8012	1171.4	−0.996	1527.2	366.0	1.03
0.8549	1179.5	−1.157	1548.9	353.4	1.75
0.9061	1184.8	−0.983	1574.7	340.4	1.53
$T = 308.15$ K					
0.0860	962.4	1.717	1362.3	559.9	−2.45
0.1287	975.0	2.450	1368.8	547.4	−3.63
0.1731	988.6	3.006	1375.6	534.5	−4.75
0.2154	999.1	3.685	1384.1	522.4	−5.68
0.2681	1014.0	4.150	1393.8	507.6	−6.57
0.3127	1027.0	4.350	1402.0	495.4	−7.05
0.3519	1038.9	4.357	1409.1	484.8	−7.27
0.4049	1055.2	4.181	1418.8	470.8	−7.27
0.4766	1078.6	3.481	1431.4	452.5	−6.64
0.5131	1090.2	3.047	1438.4	443.4	−6.11
0.5541	1103.5	2.430	1446.2	433.3	−5.34
0.5994	1117.6	1.723	1455.5	422.4	−4.33
0.6491	1133.2	0.803	1466.2	410.5	−3.07
0.6957	1146.5	0.020	1477.8	399.4	−1.85

(continued on next page)

Table 3 (*continued*)

x_1	ρ_{mix} (kg m^{-3})	V^E (cm^3 mol^{-1})	u (m sec^{-1})	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)					
0.7446	1159.2	−0.725	1491.7	387.7	−0.62
0.8012	1170.1	−1.136	1511.7	374.0	0.61
0.8549	1178.0	−1.246	1534.4	360.6	1.39
0.9061	1183.6	−1.116	1560.6	346.9	1.25
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclohexanone (2)					
T = 293.15 K					
0.0834	957.9	3.084	1450.2	496.4	−1.31
0.1328	967.9	4.322	1459.4	485.1	−2.15
0.1764	977.6	5.198	1467.2	475.2	−2.89
0.2258	994.2	5.326	1472.4	464.0	−3.68
0.2675	1009.7	5.112	1476.1	454.6	−4.28
0.3094	1026.1	4.666	1479.6	445.2	−4.82
0.3824	1055.5	3.504	1486.0	429.1	−5.51
0.4368	1077.3	2.442	1491.4	417.3	−5.78
0.4755	1092.4	1.643	1496.0	409.0	−5.87
0.5276	1111.7	0.577	1503.2	398.1	−5.84
0.5649	1124.6	−0.139	1509.3	390.4	−5.69
0.6063	1137.9	−0.867	1517.0	381.9	−5.40
0.6451	1149.3	−1.465	1525.2	374.1	−5.04
0.6947	1162.1	−2.065	1537.2	364.1	−4.48
0.7419	1172.3	−2.427	1550.5	354.8	−3.84
0.7994	1182.0	−2.556	1569.2	343.6	−2.95
0.8527	1188.4	−2.355	1589.2	333.2	−2.09
0.9134	1192.3	−1.653	1615.7	321.3	−1.16
T = 298.15 K					
0.0834	954.1	3.067	1433.6	510.0	−1.68
0.1328	965.3	4.183	1442.1	498.2	−2.64
0.1764	976.7	4.854	1448.8	487.8	−3.44
0.2258	993.2	5.015	1454.3	476.1	−4.26
0.2675	1008.8	4.794	1458.1	466.3	−4.86
0.3094	1025.1	4.371	1461.8	456.5	−5.38
0.3824	1054.3	3.254	1468.5	439.8	−6.03
0.4368	1076.3	2.177	1474.1	427.6	−6.30
0.4755	1091.7	1.342	1478.6	419.0	−6.37
0.5276	1110.9	0.303	1486.2	407.5	−6.33
0.5649	1123.8	−0.404	1492.5	399.5	−6.18
0.6063	1137.1	−1.123	1500.4	390.6	−5.90
0.6451	1148.5	−1.714	1508.9	382.4	−5.56
0.6947	1161.6	−2.344	1521.1	372.1	−5.01
0.7419	1171.8	−2.697	1534.8	362.3	−4.37
0.7994	1181.4	−2.798	1553.9	350.5	−3.47
0.8527	1187.7	−2.566	1574.3	339.7	−2.56
0.9134	1190.8	−1.728	1601.6	327.4	−1.54
T = 303.15 K					
0.0834	951.5	2.859	1413.1	526.3	−2.05
0.1328	963.3	3.921	1421.5	513.7	−3.13
0.1764	975.5	4.510	1427.9	502.8	−3.98
0.2258	992.4	4.623	1433.4	490.4	−4.84
0.2675	1007.6	4.465	1437.7	480.1	−5.45
0.3094	1024.2	4.012	1441.5	469.9	−5.95
0.3824	1053.6	2.882	1448.6	452.3	−6.60
0.4368	1075.6	1.814	1454.6	439.4	−6.83
0.4755	1091.0	0.988	1459.4	430.4	−6.90
0.5276	1110.0	−0.012	1467.5	418.3	−6.83
0.5649	1123.0	−0.727	1474.1	409.8	−6.70
0.6063	1136.2	−1.423	1482.5	400.4	−6.43
0.6451	1147.9	−2.048	1491.2	391.8	−6.08
0.6947	1160.4	−2.581	1504.3	380.8	−5.53
0.7419	1170.3	−2.878	1518.7	370.5	−4.90
0.7994	1179.8	−2.948	1538.6	358.0	−3.99
0.8527	1185.9	−2.670	1559.8	346.6	−3.03
0.9134	1188.9	−1.787	1587.9	333.6	−1.93
T = 308.15 K					
0.0834	949.1	2.624	1392.0	543.8	−2.42
0.1328	961.6	3.622	1400.2	530.4	−3.62
0.1764	974.6	4.121	1406.3	518.8	−4.54
0.2258	991.3	4.277	1412.3	505.8	−5.42
0.2675	1006.1	4.185	1417.1	494.9	−6.02
0.3094	1023.3	3.661	1420.8	484.1	−6.53
0.3824	1052.0	2.647	1428.9	465.6	−7.11
0.4368	1074.8	1.483	1434.8	452.0	−7.34
0.4755	1090.0	0.693	1440.1	442.4	−7.41
0.5276	1109.2	−0.321	1448.5	429.7	−7.34
0.5649	1122.0	−0.997	1455.6	420.6	−7.18
0.6063	1135.7	−1.753	1464.2	410.7	−6.92

Table 3 (*continued*)

x_1	ρ_{mix} (kg m^{-3})	V^E (cm^3 mol^{-1})	u (m sec^{-1})	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)					
0.6451	1147.3	−2.353	1473.4	401.5	−6.59
0.6947	1159.6	−2.845	1487.3	389.8	−6.07
0.7419	1169.5	−3.128	1502.3	378.9	−5.44
0.7994	1179.0	−3.181	1523.0	365.7	−4.50
0.8527	1185.1	−2.888	1544.8	353.6	−3.50
0.9134	1187.1	−1.831	1574.3	339.9	−2.28

Standard uncertainties, u, are u (T) (DSA) = ±0.01 K; u (ρ) = ±0.5 kg m^{-3}; u (u) = ±0.1 m s^{-1}; u (x_i) = ±1 10^{-4}; u (V^E) = ±0.1%; u (κ_S^E) = ±0.2%; u (P) = ±1000 Pa.

308.15 K and excess molar enthalpies, H^E of same set of mixtures at 298.15 K measured over entire mole fraction range are recorded in Tables 3–5 respectively. The measured ρ and u values of mixtures were employed to predict excess molar volumes, V^E and isentropic compressibilities, κ_S using:

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

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

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

The excess isentropic compressibilities, κ_S^E were estimated by employing

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

κ_S^{id} values were obtained in the manner suggested by Benson and Kiyohara [42]:

$$\kappa_S^{id} = \sum_{i=1}^{2} \varphi_i \left[\kappa_{S,i} + \frac{T v_i \alpha_i^2}{C_{P,i}}\right] - T\left(\sum_{i=1}^{2} x_i v_i\right) \frac{\left(\sum_{i=1}^{2} \varphi_i \alpha_i\right)^2}{\left(\sum_{i=1}^{2} x_i C_{P,i}\right)} \tag{4}$$

where φ_i is the volume fraction of the component (i) (i = 1 or 2) in the mixed state; $\kappa_{S,i}$, v_i, α_i and $(C_P)_i$ (i = 1 or 2) are the isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity respectively of pure component (i) (i = 1 or 2). The α value for the investigated liquids were determined using density data in the manner as described elsewhere [43].

The excess heat capacities, C_P^E, data of the present mixtures were determined using relation:

$$C_P^E = (C_P)_{mix} - \sum_{i=1}^{2} x_i (C_P)_i \tag{5}$$

where $(C_p)_{mix}$ denotes the molar heat capacities of the mixtures, $(C_p)_i$ (i = 1 or 2) are the molar heat capacities of (1) or (2) components respectively.

The excess molar enthalpies, H^E, values at desired compositions for the (1 + 2) binary mixtures were obtained directly using software supplied by the M/S SETARAM.

The V^E, κ_S^E, C_P^E and H^E data of [Bmmim][BF$_4$] (1) and cyclopentanone or cyclohexanone (2) are plotted in Figs. 1–4 and listed in Tables 3–5 respectively. To describe the composition dependence of X ($X = V$ or κ_S or C_P or H) of the mixtures, the X^E ($X = V$ or κ_S or C_P or H) of the investigated mixtures at the studied temperatures were fitted to Redlich-Kister equation [44]:

$$X^E = x_1(1-x_1)\left[X^{(0)} + X^{(1)}(2x_1-1) + X^{(2)}(2x_1-1)^2\right] \tag{6}$$

where $X^{n\ (n=0-2)}$($X = V$ or κ_S or $C_P$or H) are parameters characteristic of (1 + 2) mixtures. These parameters were determined by fitting X^E ($X = V$ or κ_S or H or C_P) data to Eq. (6) using least squares optimization. Such parameters along with standard deviations $\sigma(X^E)$ defined by:

$$\sigma\left(X^E\right) = \left\{\frac{\sum\left(X^E_{(\text{expt.})} - X^E_{\{\text{calc.equation (6)}\}}\right)^2}{(m-n)}\right\}^{0.5} \tag{7}$$

where m is the number of data points, n is the number of parameters in Eq. (6) are presented in Table 6.

4. Discussion

The ρ, u and C_P values for the investigated IL, cyclopentanone and cyclohexanone are presented in Tables 3 and 4 respectively. The comparison between experimental and literature values of ρ, u and C_P data for [Bmmim][BF$_4$] have been discussed elsewhere [45]. The experimental ρ, u and C_P values of cyclopentanone and cyclohexanone are in agreement with their literature values [28–36,40,41].

We are unaware of any V^E, κ_S^E, C_P^E and H^E data of the investigated mixtures with which to compare experimental results. While H^E data of [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures are positive; κ_S^E values are negative for [Bmmim][BF$_4$] (1) + cyclohexanone (2) mixtures across entire mole fraction range. However, sign and magnitude of V^E, C_P^E for [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) and κ_S^E for [Bmmim][BF$_4$] (1) + cyclopentanone (2) mixtures are dictated by the relative proportion of the components in mixed state.

It has been observed that ρ values (Table 3) increase with increase in concentration of IL for both mixtures. However, there is sharp rise in density values at higher concentration of IL. The small increase in density values for both mixtures at low concentration of IL in comparison to density values at high concentration may be due to weakening of cohesion forces in [Bmmim][BF$_4$] and dipole-dipole interactions in cyclopentanone or cyclohexanone in mixed state. It is also evident from the results, the densities and speeds of sound values decrease with increase in temperature.

The V^E data reflects packing effect and interaction intensity existing among the components of mixtures. The positive V^E values for [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures at mole fraction of IL, $x_{IL} \leq 0.7422$; and 0.5608 respectively, indicates least packing of cyclopentanone and cyclohexanone in the lattices of IL in comparison to mixtures at $x_{IL} > 0.7422$; and 0.5608 respectively (having negative V^E values for both mixtures) which in turn reflects strong interactions/more packing efficiency of cyclopentanone or cyclohexanone in the interstices of IL network. The V^E values of [Bmmim][BF$_4$] (1) + cyclohexanone (2) are more negative and less positive at equimolar composition than those for [Bmmim][BF$_4$] (1) + cyclopentanone (2) mixture. It may be due to reason that cyclohexanone is more basic in character and possess chair form with almost no strain and thus can be accommodated efficiently in the interstices of [Bmmim][BF$_4$] in comparison to cyclopentanone. The κ_S^E data of these mixtures also support this view point. The V^E values of [Bmim][BF$_4$] or [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures [28,46] have also been

Table 4
Measured molar heat capacities, C_p and excess heat capacities, C_P^E, values for the (1 + 2) binary mixtures as a function of mole fraction, x_1, of component (1) at T = 293.15, 298.15, 303.15 and 308.15 K and atmospheric pressure 0.1 MPa.

x_1	C_p (J K^{-1} mol^{-1})	C_P^E (J K^{-1} mol^{-1})	x_1	C_p (J K^{-1} mol^{-1})	C_P^E (J K^{-1} mol^{-1})
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)					
T = 293.15 K					
0.0918	178.11	1.28	0.5490	294.43	−1.30
0.1352	189.72	1.61	0.5987	306.70	−1.96
0.1768	200.72	1.79	0.6355	315.82	−2.41
0.2683	224.45	1.72	0.6807	327.09	−2.90
0.3044	233.64	1.52	0.7226	337.65	−3.23
0.3568	246.84	1.09	0.7734	350.68	−3.42
0.3911	255.42	0.75	0.8117	360.67	−3.39
0.4327	265.75	0.26	0.8549	372.13	−3.16
0.4832	278.22	−0.40	0.8973	383.68	−2.64
T = 298.15 K					
0.0918	179.99	1.53	0.5490	297.00	−1.05
0.1352	191.73	1.92	0.5987	309.35	−1.70
0.1768	202.82	2.13	0.6355	318.54	−2.13
0.2683	226.67	2.04	0.6807	329.92	−2.57
0.3044	235.90	1.83	0.7226	340.57	−2.88
0.3568	249.15	1.38	0.7734	353.65	−3.09
0.3911	257.77	1.02	0.8117	363.71	−3.05
0.4327	268.15	0.52	0.8549	375.24	−2.82
0.4832	280.69	−0.15	0.8973	386.79	−2.36
T = 303.15 K					
0.0918	181.48	1.71	0.5490	299.38	−0.74
0.1352	193.35	2.15	0.5987	311.84	−1.37
0.1768	204.52	2.37	0.6355	321.10	−1.79
0.2683	228.53	2.30	0.6807	332.57	−2.22
0.3044	237.83	2.09	0.7226	343.30	−2.52
0.3568	251.18	1.65	0.7734	356.47	−2.72
0.3911	259.85	1.29	0.8117	366.56	−2.71
0.4327	270.30	0.79	0.8549	378.14	−2.51
0.4832	282.94	0.14	0.8973	389.73	−2.08
T = 308.15 K					
0.0918	183.06	1.98	0.5490	301.75	−0.46
0.1352	195.06	2.48	0.5987	314.30	−1.08
0.1768	206.32	2.72	0.6355	323.66	−1.47
0.2683	230.49	2.65	0.6807	335.21	−1.89
0.3044	239.83	2.42	0.7226	346.05	−2.16
0.3568	253.25	1.96	0.7734	359.32	−2.34
0.3911	261.96	1.58	0.8117	369.48	−2.33
0.4327	272.47	1.07	0.8549	381.12	−2.14
0.4832	285.19	0.41	0.8973	392.71	−1.78
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclohexanone (2)					
T = 293.15 K					
0.1052	196.10	−4.99	0.5247	297.82	−2.63
0.1437	204.13	−6.08	0.5638	308.19	−1.52
0.1953	215.41	−7.02	0.6029	318.54	−0.43
0.2381	225.22	−7.35	0.6588	333.25	1.04
0.2827	235.82	−7.31	0.6941	342.43	1.86
0.3306	247.60	−6.88	0.7496	356.59	2.87
0.3942	263.68	−5.86	0.7967	368.27	3.39
0.4495	278.02	−4.62	0.8307	376.47	3.54
0.4880	288.12	−3.64	0.8973	391.79	3.09
T = 298.15 K					
0.1052	197.61	−5.67	0.5247	299.56	−3.45
0.1437	205.51	−6.92	0.5638	309.98	−2.33
0.1953	216.78	−7.92	0.6029	320.40	−1.20
0.2381	226.59	−8.29	0.6588	335.19	0.30
0.2827	237.17	−8.31	0.6941	344.43	1.14
0.3306	248.98	−7.89	0.7496	358.68	2.20
0.3942	265.20	−6.79	0.7967	370.45	2.77
0.4495	279.60	−5.53	0.8307	378.71	2.95
0.4880	289.81	−4.48	0.8973	394.23	2.64
T = 303.15 K					
0.1052	199.09	−6.38	0.5247	301.26	−4.24
0.1437	206.92	−7.73	0.5638	311.73	−3.09
0.1953	218.09	−8.86	0.6029	322.19	−1.96
0.2381	227.86	−9.30	0.6588	337.05	−0.43
0.2827	238.50	−9.29	0.6941	346.32	0.42
0.3306	250.36	−8.85	0.7496	360.64	1.51
0.3942	266.68	−7.70	0.7967	372.49	2.13
0.4495	281.20	−6.37	0.8307	380.82	2.35
0.4880	291.44	−5.31	0.8973	396.53	2.18

Table 4 (*continued*)

x_1	C_p (J K^{-1} mol^{-1})	C_P^E (J K^{-1} mol^{-1})	x_1	C_p (J K^{-1} mol^{-1})	C_P^E (J K^{-1} mol^{-1})
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)					
T = 308.15 K					
0.1052	200.55	−7.08	0.5247	302.74	−5.25
0.1437	208.21	−8.63	0.5638	313.29	−4.05
0.1953	219.26	−9.92	0.6029	323.85	−2.85
0.2381	229.02	−10.40	0.6588	338.82	−1.25
0.2827	239.71	−10.38	0.6941	348.18	−0.34
0.3306	251.60	−9.95	0.7496	362.62	0.83
0.3942	267.96	−8.81	0.7967	374.58	1.52
0.4495	282.56	−7.44	0.8307	383.02	1.82
0.4880	292.85	−6.36	0.8973	398.84	1.71

Standard uncertainties, u, are u (T) (DSC) = ±0.02 K; u (x_i) = ±1 10^{-4}; u (C_P^E) = ±0.3%; u (P) = ±1000 Pa.

Table 5
Measured excess molar enthalpies, H^E values for the studied mixtures as a function of mole fraction, x_1, of component (1) at T = 298.15 K and atmospheric pressure 0.1 MPa.

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)			
0.0854	10.3	0.5138	46.2
0.1296	16.1	0.5647	45.1
0.1755	21.8	0.6129	42.1
0.2248	27.8	0.6653	38.4
0.2768	34.1	0.7107	34.8
0.3264	38.7	0.7618	29.2
0.3749	42.2	0.8122	22.8
0.4251	44.8	0.8681	15.7
0.4699	46.1	0.9145	9.90
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclohexanone (2)			
0.0714	20.8	0.5274	73.9
0.1128	31.8	0.5761	71.0
0.1647	43.7	0.6233	66.7
0.2156	52.8	0.6759	60.4
0.2628	60.2	0.7253	53.3
0.3142	66.6	0.7711	45.0
0.3659	72.2	0.8237	35.5
0.4128	74.6	0.8762	25.8
0.4766	75.3	0.9227	16.2

Standard uncertainties, u, are u (T) (DSC) = ±0.02 K; u (x_i) = ±1 10^{-4}; u (H^E) = ±1%; u (P) = ±1000 Pa.

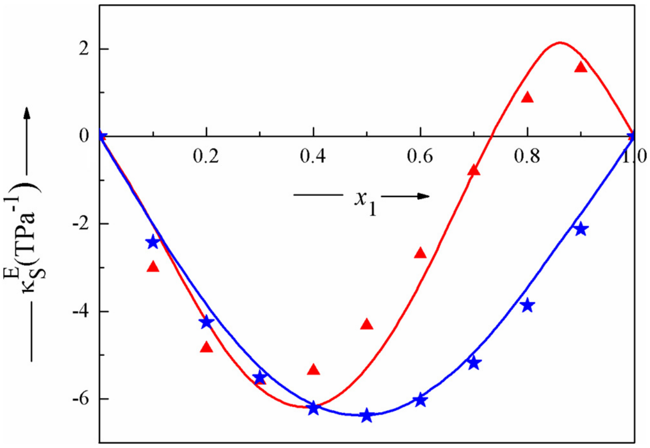


Fig. 2. Excess isentropic compressibilities, $(\kappa_S^E)_{12}$ for (I) [Bmmim][BF$_4$] (1) + cyclopentanone (2) Expt. (—); Graph (▲) (II) [Bmmim][BF$_4$] (1) + cyclohexanone (2) Expt. (—); Graph (★) at 298.15 K.

compared with the V^E values of the studied mixtures. It has been observed that V^E values for these mixtures at equimolar composition follow the order: [Bmmim][BF$_4$] > [Bmim][BF$_4$] > [Emim][BF$_4$]. It may be due to the presence of bulky –CH$_3$ group/s in [Bmim][BF$_4$] or [Bmmim][BF$_4$] which restricts the approach of cyclopentanone or cyclohexanone molecules in the interstices of [Bmim][BF$_4$] or [Bmmim][BF$_4$] network. The $\partial V^E/\partial T$ and $\partial(\kappa_S^E)/\partial T$ for the present mixtures are negative. This may be due to increase in disruption of cohesion forces in IL or dipole-dipole interactions in cyclopentanone or cyclohexanone with increase in temperature, which in turn leads to a more packed structure.

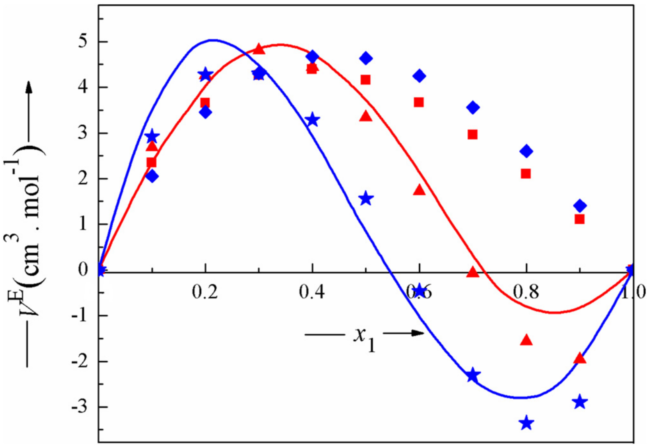


Fig. 1. Excess molar volumes, V^E_{12} for (I) [Bmmim][BF$_4$] (1) + cyclopentanone (2) Expt. (—); Graph/$_{Eq.}$ (8) (■), Graph/$_{Eq.}$ (14) (▲) (II) [Bmmim][BF$_4$] (1) + cyclohexanone (2) Expt. (—); Graph/$_{Eq.}$(8) (♦), Graph/$_{Eq.}$ (14) (★) at 298.15 K.

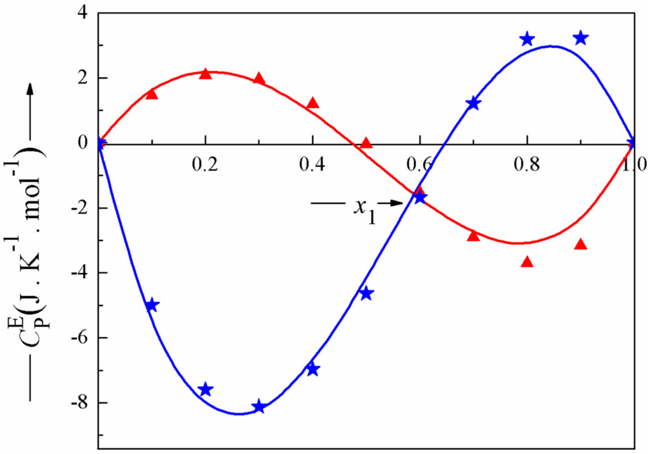


Fig. 3. Excess molar enthalpies, H^E_{12} for (I) [Bmmim][BF$_4$] (1) + cyclopentanone (2) Expt. (—); Graph (▲) (II) [Bmmim][BF$_4$] (1) + cyclohexanone (2) Expt. (—) Graph (★) at 298.15 K.

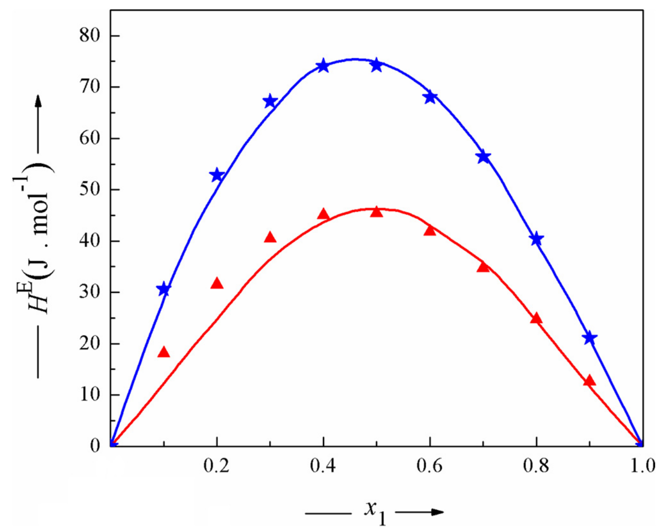


Fig. 4. Excess heat capacities, $(C_P^E)_{12}$ for (I) [Bmmim][BF$_4$] (1) + cyclopentanone (2) Expt. (—); Graph (▲) (II) [Bmmim][BF$_4$] (1) + cyclohexanone (2) Expt. (—); Graph (★) at 298.15 K.

The positive C_P^Evalues for [Bmmim][BF$_4$] (1) + cyclopentanone (2) mixture have been observed at low IL mole fraction, $x_{IL} \leq 0.4532$ which in turn changes to negative at $x_{IL} > 0.4532$. However, reverse is the case for [Bmmim][BF$_4$] (1) + cyclohexanone (2) mixture. For [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2), the negative C_P^E suggest that contribution to C_P^E due to rupture of cohesion forces in IL; and dipole-dipole interactions in cyclopentanone or cyclohexanone far outweigh the contribution due to interactions between IL and cyclopentanone or cyclohexanone to form 1:2 molecular complex possessing compact (non-random) structure while the positive suggest otherwise. The $\partial(C_P^E)/\partial T$ for [Bmmim][BF$_4$] (1) + cyclopentanone (2) mixture is positive which suggests compact structure in mixed state due to more interactions among the unlike molecules in comparison to like molecules. However, $\partial(C_P^E)/\partial T$ for [Bmmim][BF$_4$] (1) + cyclohexanone (2) mixture is negative which indicates the opposite view point. The C_P^E values of [Bmim][BF$_4$] or [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) have been reported in the literature [28,46] and for [Bmmim][BF$_4$] or [Bmim][BF$_4$] or [Emim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures at equimolar composition vary in the order: [Bmim][BF$_4$] > [Emim][BF$_4$] > [Bmmim][BF$_4$]; and [Bmim][BF$_4$] > [Bmmim][BF$_4$] > [Emim][BF$_4$] respectively. The C_P^E data for [Bmmim][BF$_4$] or [Bmim][BF$_4$] or [Emim][BF$_4$] (1) + cyclopentanone (2) mixtures suggest least interactions/packing of cyclopentanone molecules with [Bmmim][BF$_4$] in comparison to [Bmim][BF$_4$] or [Emim][BF$_4$] which in turn leads [Bmmim][BF$_4$]:cyclopentanone molecular complex possessing least non-random structure. These observations are consistent with the information inferred from the analysis of their V^E data. This view point also support the C_P^E data of [Bmmim][BF$_4$] or [Bmim][BF$_4$] or [Emim][BF$_4$] (1) + cyclohexanone (2) mixtures.

The excess molar enthalpies, H^E data of liquid mixtures is related to the net destruction and creation of interactions among the components of mixtures in the mixed state. The sign and magnitude of H^E data roughly reflects the balance between the interactions among like and unlike species in mixtures. The H^E data of studied mixtures may be explained qualitatively, if it be assumed that (i) [Bmmim][BF$_4$] is characterized by cohesion forces and exists as a monomer; cyclopentanone and cyclohexanone are characterized by dipole-dipole interactions and exist as associated molecular entities; (ii) the addition of (1) to (2) or vice-versa rupture cohesion forces in IL and cyclopentanone or cyclohexanone to form (1) and (2) monomers; and (iii) monomers of the molecules undergo interactions to form 1:2 molecular complex. The positive H^E data of (1 + 2) mixtures suggest contribution to H^E due to factor (ii) far outweigh contribution due to factor (iii). The H^E values of [Bmmim][BF$_4$] (1) + cyclohexanone (2) mixture are higher than those for [Bmmim][BF$_4$] (1) + cyclopentanone (2) mixture in spite of the fact that cyclohexanone is more basic in character than cyclopentanone and thus must interact strongly with [Bmmim][BF$_4$]. It may be due to high dielectric constant of cyclohexanone at 298.15 K ($\varepsilon_s = 15.77$) in comparison to cyclopentanone ($\varepsilon_s = 13.49$) [47] which in turn yields strong dipole-dipole interactions in cyclohexanone and thus require more energy to rupture these interactions. The comparison of H^E data for [Bmmim][BF$_4$] or [Bmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures has revealed that H^E values for [Bmmim][BF$_4$] or [Bmim][BF$_4$] (1) + cyclohexanone (2) mixtures (at equimolar composition) are higher than [Bmmim][BF$_4$] or [Bmim][BF$_4$] (1) + cyclopentanone (2) mixtures. It may be due to high dielectric constant value of cyclohexanone.

5. Graph theory

The Graph theory has been successfully utilized [48–51] to relate structure of a molecule with its physical and chemical properties; and

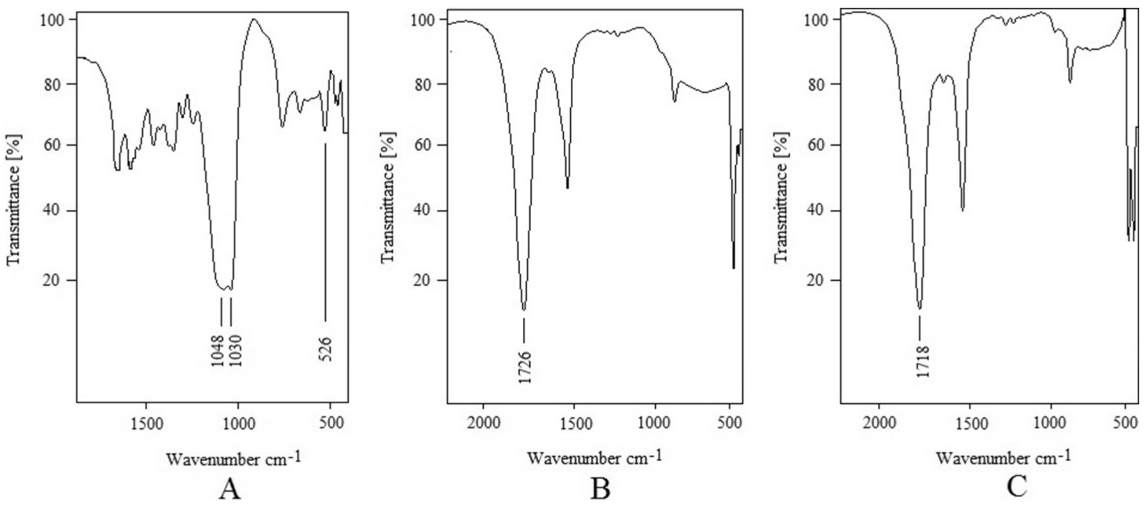


Fig. 5. FT-IR spectra of pure (A) [Bmmim][BF$_4$], (B) Cyclopentanone and (C) Cyclohexanone.

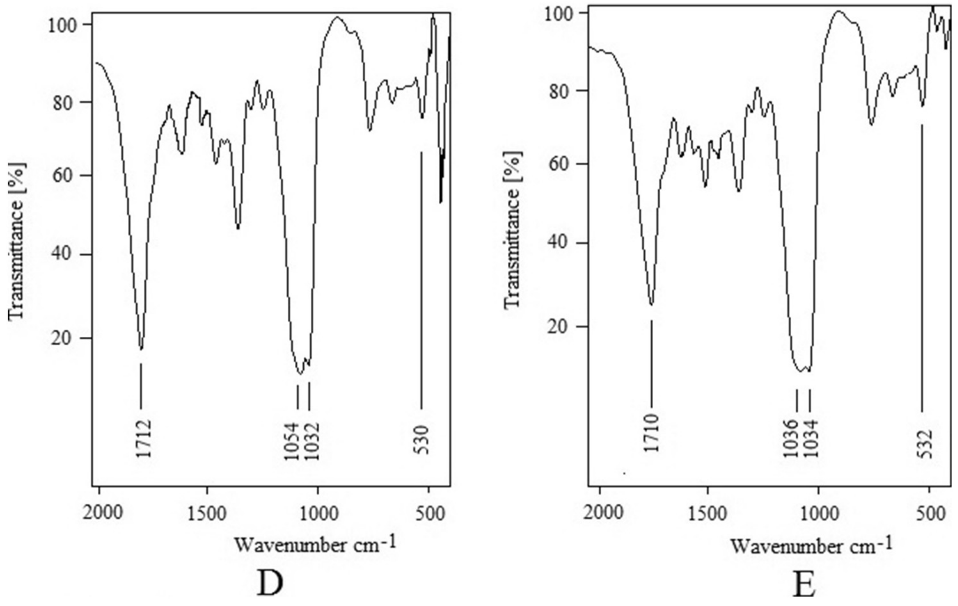


Fig. 6. FT-IR spectra of equimolar (D) [Bmmim][BF$_4$] (1) + cyclopentanone (2) and (E) [Bmmim][BF$_4$] (1) + cyclohexanone (2) mixtures.

connectivity parameter of third degree of a molecule (derived from their topology) with thermodynamic properties like V^E, κ_S^E, C_p^E and H^E of the mixtures. Excess molar volume, V^E is a packing effect and addition of (1) to (2) would cause change in topology. It was, therefore, of interest to analyze V^E of the investigated mixtures in terms of Graph theory to obtain information about the state of components in pure and mixed state.

Table 6
Binary adjustable parameters, X^n ($\sigma(X^E)$ ($X = V$ or κ_S or C_P or H; n = 0–2) of Eq. (6) along with their standard deviations, $\sigma(X^E)$ ($X = V$ or κ_S or C_P or H) at T = 293.15, 298.15, 303.15 and 308.15 K.

Parameters	T/K			
	293.15	298.15	303.15	308.15
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)				
$V^{(0)}$	15.600	14.763	13.729	12.841
$V^{(1)}$	−26.383	−25.738	−25.300	−24.874
$V^{(2)}$	−11.990	−13.385	−14.634	−15.848
$\sigma(V^E)$/cm^3 mol^{-1}	0.002	0.002	0.002	0.002
$\kappa_S^{(0)}$	−19.14	−21.20	−23.24	−25.28
$\kappa_S^{(1)}$	28.78	29.42	30.19	30.95
$\kappa_S^{(2)}$	37.49	34.64	31.70	28.75
$\sigma(\kappa_S^E)$/TPa^{-1}	0.00	0.01	0.01	0.01
$C_p^{(0)}$	−2.50	−1.51	−0.35	0.74
$C_p^{(1)}$	−27.40	−27.36	−26.81	−26.69
$C_p^{(2)}$	−6.90	−3.66	−1.54	1.76
$\sigma(C_p^E)$/J K^{-1} mol^{-1}	0.00	0.00	0.00	0.00
$H^{(0)}$	–	184	–	–
$H^{(1)}$	–	−3.10	–	–
$H^{(2)}$	–	−80.0	–	–
$\sigma(H^E)$/J mol^{-1}	–	0.27	–	–
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclohexanone (2)				
$V^{(0)}$	4.795	3.665	2.284	1.123
$V^{(1)}$	−40.385	−40.346	−39.574	−39.151
$V^{(2)}$	8.434	7.499	7.281	5.359
$\sigma(V^E)$/cm^3 mol^{-1}	0.002	0.002	0.002	0.002
$\kappa_S^{(0)}$	−23.52	−25.50	−27.57	−29.55
$\kappa_S^{(1)}$	1.75	1.99	2.26	2.49
$\kappa_S^{(2)}$	11.37	7.47	3.76	−0.15
$\sigma(\kappa_S^E)$/TPa^{-1}	0.01	0.01	0.01	0.01
$C_p^{(0)}$	−13.23	−16.63	−19.89	−23.98
$C_p^{(1)}$	54.59	56.22	57.81	60.08
$C_p^{(2)}$	5.16	1.09	−3.71	−6.41
$\sigma(C_p^E)$/J K^{-1} mol^{-1}	0.01	0.01	0.01	0.02
$H^{(0)}$	–	297	–	–
$H^{(1)}$	–	−53.1	–	–
$H^{(2)}$	–	−37.5	–	–
$\sigma(H^E)$/J mol^{-1}	–	0.53	–	–

According to Graph theory, V^E is given by

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

where x_1 is the mole fraction of component (1) and α_{12} is a constant characteristic of (1 + 2) mixture. The ($^3\xi_i$) (i = 1 or 2); ($^3\xi_i$)$_m$(i = 1 or 2) are connectivity parameters of third degree of the constituent molecules and are defined by

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

where δ_m^{ν} etc. has same significance as explained elsewhere [52]. The ($^3\xi_i$) (i = 1 or 2); ($^3\xi_i$)$_m$(i = 1 or 2) parameters of the components of the mixtures were estimated by fitting experimental V^E data to Eq. (8); and only those values were considered that best reproduced the V^E data. Such V^E values along with ($^3\xi_i$) (i = 1 or 2); ($^3\xi_i$)$_m$(i = 1 or 2) are listed in Tables 7 and 8 respectively. Examination of data in Table 7; reveals that V^E values are comparable to experimental values at $x_1 \le 0.7$ and ≤0.5 for [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures respectively. The failure of theory to correctly predict the sign of V^E values at $x_1 > 0.7$; and >0.5 for [Bmmim][BF$_4$] (1) + cyclopentanone or cyclohexanone (2) mixtures respectively may be due to fact that α_{12} parameter has estimated by employing V^E values at one composition. However, ($^3\xi_i$) (i = 1 or 2); ($^3\xi_i$)$_m$(i = 1 or 2) values may be used to predict the state of components (1) and (2) in pure as well as mixed state.

Structures were assumed for [Bmmim][BF$_4$], cyclopentanone, cyclohexanone and their ($^3\xi'$) values {predicted by structural consideration i.e. Eq. (9) were determined. Any structure or combination of the structures of component yielded ($^3\xi'$) values comparable to ($^3\xi$) value was taken to be structure of that component. We assumed that [Bmmim][BF$_4$], cyclopentanone and cyclohexanone exist as molecular entities I, II–IV and V–VII respectively. In evaluating ($^3\xi'$) value for [Bmmim][BF$_4$], it was assumed that (i) [BF$_4$]$^-$ is positioned over the imidazolium ring of [Bmmim][BF$_4$]; and (ii) cohesion forces exist between proton of –CH$_3$ groups of imidazolium ring and fluorine atoms of [BF$_4$]$^-$. The ($^3\xi'$) values for molecular entities I–VII were then

Table 7
Comparison of measured V^E, κ_S^E, C_p^E values from appropriate equations with their corresponding experimental values at $T = 293.15$, 298.15, 303.15 and 308.15 K and H^E at $T = 298.15$ K.

Properties	Mole fraction of component (1), x_1								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)									
$T = 293.15$ K									
V^E (Expt.)	2.502	4.403	5.198	4.898	3.901	2.301	0.481	−0.952	−1.404
V^E(Graph)$_{\text{Eq. (8)}}$	2.615	4.073	4.758	4.898	4.642	4.087	3.303	2.338	1.228
V^E(Graph) $_{\text{Eq. (14)}}$	2.836	4.540	5.198	4.927	3.887	2.299	0.481	−1.088	−1.661
κ_S^E(Expt.)	−1.71	−3.50	−5.12	−5.71	−4.89	−2.90	−0.31	1.89	2.51
κ_S^E(Graph)	−2.81	−4.49	−5.12	−4.82	−3.75	−2.14	−0.31	1.24	1.77
C_p^E(Expt.)	1.18	2.05	1.96	0.73	−0.62	−2.24	−3.21	−3.45	−2.51
C_p^E(Graph)	1.18	1.61	1.37	0.59	−0.60	−1.97	−3.21	−3.86	−3.19
$T = 298.15$ K									
V^E (Expt.)	2.297	4.012	4.802	4.390	3.304	1.701	−0.072	−1.399	−1.703
V^E(Graph)$_{\text{Eq. (8)}}$	2.344	3.651	4.264	4.390	4.160	3.663	2.960	2.095	1.101
V^E(Graph) $_{\text{Eq. (14)}}$	2.687	4.257	4.802	4.441	3.339	1.725	−0.072	−1.558	−1.960
κ_S^E(Expt.)	−2.10	−4.12	−5.59	−6.22	−5.41	−3.49	−0.80	1.51	2.20
κ_S^E(Graph)	−3.01	−4.85	−5.59	−5.36	−4.32	−2.69	−0.80	0.86	1.55
C_p^E(Expt.)	1.46	2.40	2.19	1.03	−0.34	−1.92	−2.91	−3.14	−2.22
C_p^E(Graph)	1.46	2.08	1.95	1.18	−0.05	−1.53	−2.91	−3.71	−3.17
H^E (Expt.)	12.2	25.1	36.9	45.0	47.2	41.8	33.1	23.3	12.0
H^E (Graph)	18.1	31.5	40.5	45.0	45.4	41.8	34.7	24.7	12.6
$T = 303.15$ K									
V^E (Expt.)	2.101	3.650	4.402	4.002	2.810	1.101	−0.604	−1.803	−1.897
V^E(Graph)$_{\text{Eq. (8)}}$	2.137	3.328	3.887	4.002	3.793	3.340	2.699	1.910	1.003
V^E(Graph) $_{\text{Eq. (14)}}$	2.533	3.969	4.402	3.956	2.799	1.166	−0.604	−2.004	−2.240
κ_S^E(Expt.)	−2.52	−4.69	−6.20	−6.69	−5.90	−4.03	−1.31	1.09	1.89
κ_S^E(Graph)	−3.29	−5.33	−6.20	−6.04	−5.00	−3.31	−1.31	0.51	1.37
C_p^E(Expt.)	1.62	2.73	2.40	1.34	0.06	−1.59	−2.62	−2.81	−1.93
C_p^E(Graph)	1.62	2.36	2.30	1.57	0.34	−1.17	−2.62	−3.51	−3.07
$T = 308.15$ K									
V^E (Expt.)	1.802	3.401	4.011	3.604	2.303	0.620	−0.981	−2.112	−2.105
V^E(Graph)$_{\text{Eq. (8)}}$	1.924	2.997	3.501	3.604	3.415	3.007	2.430	1.720	0.904
V^E(Graph) $_{\text{Eq. (14)}}$	2.363	3.669	4.011	3.512	2.340	0.730	−0.981	−2.287	−2.396
κ_S^E(Expt.)	−2.90	−5.31	−6.79	−7.20	−6.42	−4.51	−1.82	0.68	1.61
κ_S^E(Graph)	−3.55	−5.78	−6.79	−6.69	−5.66	−3.92	−1.82	0.15	1.19
C_p^E(Expt.)	1.91	3.04	2.73	1.61	0.30	−1.33	−2.29	−2.52	−1.60
C_p^E(Graph)	1.91	2.84	2.90	2.20	0.91	−0.70	−2.29	−3.34	−3.03
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclohexanone (2)									
$T = 293.15$ K									
V^E (Expt.)	4.011	5.302	4.897	3.203	1.105	−0.899	−2.107	−2.502	−1.901
V^E(Graph)$_{\text{Eq. (8)}}$	2.343	3.936	4.897	5.320	5.280	4.841	4.053	2.961	1.599
V^E(Graph) $_{\text{Eq. (14)}}$	3.243	4.790	4.897	3.866	2.054	−0.110	−2.107	−3.306	−2.927
κ_S^E(Expt.)	−1.59	−3.20	−4.71	−5.71	−6.03	−5.50	−4.29	−2.80	−1.42
κ_S^E(Graph)	−2.23	−3.92	−5.07	−5.71	−5.85	−5.50	−4.71	−3.50	−1.91
C_p^E(Expt.)	−4.82	−7.11	−7.20	−5.82	−3.29	−0.52	2.03	3.52	3.04
C_p^E(Graph)	−4.59	−6.88	−7.20	−5.95	−3.60	−0.71	2.03	3.79	3.54
$T = 298.15$ K									
V^E (Expt.)	3.604	4.801	4.301	2.595	0.603	−1.207	−2.300	−2.698	−2.102
V^E(Graph)$_{\text{Eq. (8)}}$	2.057	3.457	4.301	4.672	4.638	4.252	3.560	2.600	1.405
V^E(Graph) $_{\text{Eq. (14)}}$	2.921	4.275	4.301	3.284	1.561	−0.463	−2.300	−3.355	−2.893
κ_S^E(Expt.)	−2.04	−3.81	−5.29	−6.22	−6.50	−6.03	−4.80	−3.31	−1.79
κ_S^E(Graph)	−2.42	−4.25	−5.52	−6.22	−6.39	−6.03	−5.18	−3.87	−2.12
C_p^E(Expt.)	−5.50	−8.03	−8.12	−6.62	−4.21	−1.39	1.21	2.89	2.61
C_p^E(Graph)	−5.00	−7.60	−8.12	−6.97	−4.64	−1.68	1.21	3.19	3.22
H^E (Expt.)	28.1	50.9	67.2	75.0	74.2	67.3	56.1	40.0	20.8
H^E (Graph)	30.6	52.8	67.2	74.1	74.2	68.0	56.4	40.4	21.1
$T = 303.15$ K									
V^E (Expt.)	3.207	4.305	3.606	2.004	0.204	−1.502	−2.503	−2.798	−2.202
V^E(Graph)$_{\text{Eq. (8)}}$	1.725	2.898	3.606	3.917	3.888	3.565	2.985	2.180	1.178
V^E(Graph) $_{\text{Eq. (14)}}$	2.543	3.671	3.606	2.611	0.999	−0.856	−2.503	−3.390	−2.838
κ_S^E(Expt.)	−2.41	−4.39	−5.91	−6.79	−7.04	−6.51	−5.32	−3.79	−2.21
κ_S^E(Graph)	−2.67	−4.68	−6.05	−6.79	−6.93	−6.51	−5.55	−4.11	−2.24
C_p^E(Expt.)	−6.31	−8.80	−9.07	−7.51	−5.09	−2.26	0.42	2.19	2.20
C_p^E(Graph)	−5.44	−8.35	−9.07	−8.02	−5.68	−2.63	0.42	2.62	2.92
$T = 308.15$ K									
V^E (Expt.)	2.803	3.797	3.011	1.503	0.051	−1.802	−2.697	−3.002	−2.404
V^E(Graph)$_{\text{Eq. (8)}}$	1.440	2.420	3.011	3.271	3.247	2.976	2.492	1.820	0.983
V^E(Graph) $_{\text{Eq. (14)}}$	2.223	3.157	3.011	2.031	0.507	−1.209	−2.697	−3.441	−2.805
κ_S^E(Expt.)	−2.80	−5.03	−6.49	−7.32	−7.50	−7.02	−5.81	−4.32	−2.60
κ_S^E(Graph)	−2.88	−5.05	−6.52	−7.32	−7.48	−7.02	−5.99	−4.44	−2.42
C_p^E(Expt.)	−7.02	−9.79	−10.03	−8.42	−6.10	−3.17	−0.43	1.48	1.85
C_p^E(Graph)	−5.87	−9.09	−10.03	−9.09	−6.76	−3.64	−0.43	2.00	2.59

Table 8

The connectivity parameters of third degree of a molecule, $(^3\xi_1)$, $(^3\xi_1)_m$ and $(^3\xi_2)$, $(^3\xi_2)_m$ along with interaction energy parameters χ^*, $\chi^{/}_{12}$ and α_{12} utilized in Graph theory for the prediction of V^E, κ_S^E and C_P^E at T = 293.15, 298.15, 303.15, 308.15 K and H^E at T = 298.15 K. Also included are the deviations between the experimental and calculated values by Graph theory, $\sigma(V^E{}_{Graph})$, $\sigma(\kappa_S^E{}_{Graph})$, $\sigma(H^E{}_{Graph})$ and $\sigma(C_P{}^E{}_{Graph})$.

Parameters	T/K			
	293.15	298.15	303.15	308.15
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone (2)				
$(^3\xi_1) = (^3\xi_1)_m$	3.403	3.403	3.403	3.403
$(^3\xi_2) = (^3\xi_2)_m$	1.287	1.287	1.287	1.287
α_{12}/cm^3 mol^{-1}	−42.588	−38.171	−34.797	−31.337
$\sigma(V^E{}_{Graph})$/Eq. (8)	2.062	2.213	2.374	2.471
$\chi^{/v}_{12}$/cm^3 mol^{-1}	17.133	16.349	15.529	14.584
χ^{*v}/cm^3 mol^{-1}	−14.985	−15.319	−15.580	−15.427
$\sigma(V^E{}_{Graph})$/Eq. (14)	0.176	0.210	0.254	0.274
$\chi^{/\kappa}_{12}$/TPa^{-1}	−17.04	−18.14	−19.70	−21.18
$\chi^{*\kappa}$/TPa^{-1}	15.22	15.30	15.78	16.17
$\sigma(\kappa_S{}^E{}_{Graph})$	0.91	0.83	0.69	0.57
$\chi^{/C_P}_{12}$/J K^{-1} mol^{-1}	7.89	9.53	10.43	12.12
χ^{*C_P}/J K^{-1} mol^{-1}	−13.49	−14.44	−14.72	−15.66
$\sigma(C_P{}^E{}_{Graph})$	0.43	0.49	0.57	0.75
$\chi^{/H}_{12}$/J mol^{-1}	–	102	–	–
χ^{*H}/J mol^{-1}	–	−28.1	–	–
$\sigma(H^E{}_{Graph})$	–	3.72	–	–
1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclohexanone (2)				
$(^3\xi_1) = (^3\xi_1)_m$	3.403	3.403	3.403	3.403
$(^3\xi_2) = (^3\xi_2)_m$	2.105	2.105	2.105	2.105
α_{12}/cm^3 mol^{-1}	−247.310	−217.211	−182.111	−152.063
$\sigma(V^E{}_{Graph})$/Eq. (8)	4.465	4.298	4.025	3.809
$\chi^{/v}_{12}$/cm^3 mol^{-1}	20.827	18.881	16.582	14.640
χ^{*v}/cm^3 mol^{-1}	−24.593	−23.267	−21.638	−20.319
$\sigma(V^E{}_{Graph})$/Eq. (14)	0.803	0.732	0.656	0.526
$\chi^{/\kappa}_{12}$/TPa^{-1}	−12.56	−13.57	−15.05	−16.21
$\chi^{*\kappa}$/TPa^{-1}	−0.09	−0.32	0.13	0.12
$\sigma(\kappa_S{}^E{}_{Graph})$	0.54	0.37	0.22	0.11
$\chi^{/C_P}_{12}$/J K^{-1} mol^{-1}	−29.22	−31.55	−34.02	−36.45
χ^{*C_P}/J K^{-1} mol^{-1}	32.20	32.31	32.63	32.77
$\sigma(C_P{}^E{}_{Graph})$	0.29	0.43	0.59	0.73
$\chi^{/H}_{12}$/J mol^{-1}	–	174	–	–
χ^{*H}/J mol^{-1}	–	−20.9	–	–
$\sigma(H^E{}_{Graph})$	–	1.28	–	–

calculated to be 3.199, 0.984, 1.347, 1.386, 1.411, 1.597, 1.935 respectively (Scheme 1). The $(^3\xi)$ values of 3.403, 1.287, 2.105 [Bmmim][BF$_4$], cyclopentanone, cyclohexanone (Table 8) suggests that [Bmmim][BF$_4$] exists as monomer (molecular entity I; $^3\xi^{/}$= 3.199) cyclopentanone (molecular entities III-IV; $^3\xi^{/}$ = 1.368) and cyclohexanone (molecular entities VI-VII; $^3\xi^{/}$ = 1.761) exist as a mixture of open and cyclic dimer. The information regarding nature and extent of interactions along with molecular entities existing in the mixtures was then obtained by predicting the value of connectivity parameter of third degree for molecular entities of [Bmmim][BF$_4$] in cyclopentanone or cyclohexanone $(^3\xi^{/}_1)_m$. For this purpose, we assumed that present (1 + 2) mixtures may possess molecular entities VIII and IX in mixed state. The connectivity parameters of third degree, $(^3\xi^{/})_m$ in the mixed state for the proposed molecular entities VIII-IX were determined {via structural consideration (Eq. (9)} by assuming that proposed molecular entities are characterized by interactions between

hydrogen and oxygen atom of cyclopentanone or cyclohexanone with fluorine atom of [BF$_4$]$^-$ anion and proton of –CH$_3$ groups attached to imidazolium ring of [Bmmim]$^+$ cation. The $(^3\xi^{/})_m$ value for molecular entities VIII–IX was then estimated to be 3.620. The $(^3\xi)_m$ value of 3.403 (Table 8) in the presented mixtures support the existence of molecular entities VIII-IX in the mixtures.

The presence of molecular entities VIII–IX inferred that addition of cyclopentanone or cyclohexanone to [Bmmim][BF$_4$] must influence (i) B—F stretching of [BF$_4$]$^-$ anion; (ii) in plane bending vibration of –CH$_3$ groups in [Bmmim][BF$_4$]; and (iii) > C = O vibrations of cyclopentanone or cyclohexanone. For this purpose, we analyzed the IR spectral data of pure [Bmmim][BF$_4$], cyclopentanone, cyclohexanone and their equimolar (1 + 2) mixtures. It was observed that [Bmmim][BF$_4$], cyclopentanone, cyclohexanone showed characteristic vibrations [53,54] at 526 cm^{-1} (B—F stretching); 1048, 1030 cm^{-1} (in plane bending vibrations of –CH$_3$) and; 1726, 1718 cm^{-1} (>C = O vibrations of cyclopentanone or cyclohexanone) shown in Fig. 5 which in turn were shifted to; 530, 532 cm^{-1} (B—F stretching); 1054, 1032; 1034, 1036 cm^{-1} (in plane bending vibrations of –CH$_3$) and; 1712; 1710 cm^{-1} (>C = O vibrations of cyclopentanone or cyclohexanone) presented in Fig. 6. The analysis of IR spectral data of mixtures thus supports the presence of molecular entities VIII–IX in the studied mixtures.

Quantum mechanical calculations using density functional theory [55–57] were performed to support the presence of proposed molecular entities in pure and mixed states. For this purpose, the full optimization of structures of [Bmmim][BF$_4$], cyclopentanone and cyclohexanone in pure as well as mixed states were performed with Gaussian program package 09 which carried out on the B3LYP/6–311++G (d, p) level of theory [58,59]. The estimated inter-nuclear distances among interacting atoms in pure [Bmmim][BF$_4$], cyclopentanone, cyclohexanone (molecular entities I–VII) and mixed states (molecular entities VIII–IX) are labelled in Scheme 1. The inter-nuclear distances of 2.24 A° and 3.37 A° between proton of –CH$_3$ group attached to carbon (C$_2$) of imidazolium ring and fluorine atoms of [BF$_4$]$^-$; and 2.26 A° between proton of –CH$_3$ group attached to nitrogen atom of imidazolium ring of [Bmmim]$^+$ with fluorine atom of [BF$_4$]$^-$ suggest interactions between proton of –CH$_3$ group attached to carbon (C$_2$) of imidazolium ring and proton of –CH$_3$ group attached to nitrogen atom of imidazolium ring of [Bmmim]$^+$ with fluorine atoms of [BF$_4$]$^-$ (molecular entity I). Further, inter-nuclear distance of 3.16 A° and 3.19 A° between carbon and oxygen atoms of cyclopentanone (molecular entities III–IV); and cyclohexanone (molecular entities VI–VII) respectively advocated the presence of open and cyclic dimer. In mixed states (molecular entities VIII–IX), the inter-nuclear distances between (i) the proton of –CH$_3$

group attached to carbon (C_2) of imidazolium ring $[\mathrm{Bmmim}]^+$ with oxygen atom of cyclopentanone or cyclohexanone; (ii) proton of $-CH_3$ group attached to nitrogen atom of imidazolium ring of $[\mathrm{Bmmim}]^+$ with oxygen atom of cyclopentanone or cyclohexanone; (iii) proton of cyclopentanone or cyclohexanone with fluorine atom of $[BF_4]^-$ (iv) nitrogen atom of $[\mathrm{Bmmim}]^+$ with fluorine atom of $[BF_4]^-$ were found to be 3.34 A°, 2.79 A°; 2.56 A°, 2.59 A°; 2.60 A°, 2.68 A°; and 3.01 A°, 3.02 A° respectively. These inter-nuclear distances supported the presence of molecular entities VIII–IX in the mixed states. The quantum mechanical calculations thus also support the various assumptions made in evaluating the connectivity parameters of third degree, $^3\xi^{/}$ for the various molecular entities in pure as well as mixed states which in turn have been utilized to determine V^E, κ_S^E, C_P^E and H^E of the studied mixtures.

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

Topological, thermodynamical analysis of V^E, κ_S^E, C_P^E and H^E data for [Bmmim][BF_4] (1) + cyclopentanone or cyclohexanone (2) mixtures and also their quantum mechanical calculations/IR spectral studies have indicated that while [Bmmim][BF_4] is characterized by cohesion forces and exists as monomer; cyclopentanone and cyclohexanone exist as associated molecular entities (2_n-2_n dipole interactions). The addition of component (1) to (2) leads to form (1 + 2) binary mixture and may be assumed to involve processes, (i) establishment of 1-2_n contacts; (ii) unlike contact formation in turn results in rupture of (a) cohesion forces in [Bmmim][BF_4]; (b) dipole-dipole interactions (2_n-2_n) in cycloalkanones to yield their respective monomers and results in increase in randomness; (iii) monomers of constituent molecules then undergo specific interactions to form non-random 1:2 molecular complex. If χ_{12}, χ_1, χ_2, χ^*_{12} are molar volumes, molar compressibility, molar interaction parameters for formation of unlike 1–2 contacts; breakdown of (a) cohesion forces in [Bmmim][BF_4]; and (b) associated entities (2_n-2_n dipole interactions) and increase in randomness; and molecular interactions among (1) and (2) to form 1:2 molecular complex; and decrease randomness respectively; then change in thermodynamic properties, $\Delta X(X = V or \kappa_S or C_P or H)$ due to processes (i–iii) were expressed [60–62]

$$\Delta X_{\mathrm{i}}(X = V\,or\,\kappa_S\,or\,C_P\,or\,H) = \left[\frac{x_1x_2(^3\xi_1/^3\xi_2)}{x_1+x_2(^3\xi_1/^3\xi_2)}\right][\chi_{12}] \tag{10}$$

$$\Delta X_{\mathrm{ii}}(X = V\,or\,\kappa_S\,or\,C_P\,or\,H) = \left[\frac{x_1^2x_2(^3\xi_1/^3\xi_2)}{x_1+x_2(^3\xi_1/^3\xi_2)}\right][\chi_1+\chi_2] \tag{11}$$

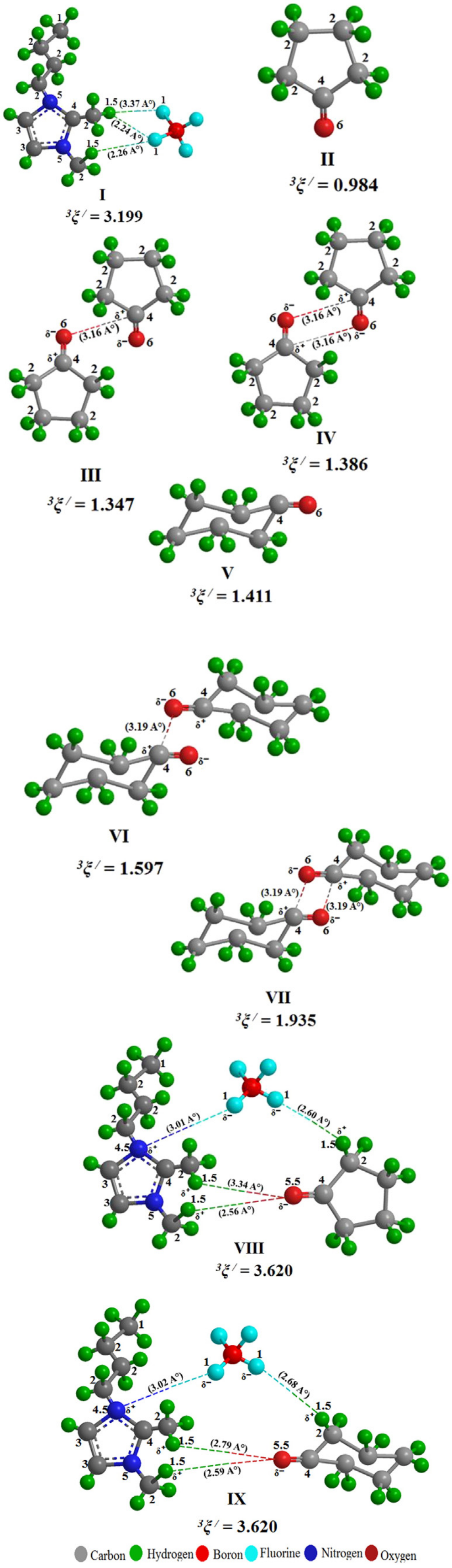
$$\Delta X_{\mathrm{iii}}(X = V\,or\,\kappa_S\,or\,C_P\,or\,H) = \left[\frac{x_1x_2^2(^3\xi_1/^3\xi_2)}{x_1+x_2(^3\xi_1/^3\xi_2)}\right][\chi^*_{12}] \tag{12}$$

The total change in the thermodynamic properties, $X^E(X = V or \kappa_S or C_P or H)$ for the studied (1 + 2) mixtures due to processes (i–iii) were, expressed by

$$X^E(X = V\,or\,\kappa_S\,or\,C_P\,or\,H) = \sum_{\mathrm{i=i}}^{\mathrm{iii}}(\Delta X_{\mathrm{i}}) = \left[\frac{x_1x_2(^3\xi_1/^3\xi_2)}{x_1+x_2(^3\xi_1/^3\xi_2)}\right]\left[\chi_{12}+x_1\chi_1+x_1\chi_2+x_2\chi^*_{12}\right] \tag{13}$$

For the investigated mixtures, we assumed that $\chi_{12} \cong \chi^*_{12} = \chi^{/}_{12}$ and $\chi_1 \cong \chi_2 = \chi^*$, Eq. (13) was, therefore, reduced to:

$$X^E(X = V\,or\,\kappa_S\,or\,H\,or\,C_P) = \left[\frac{x_1x_2(^3\xi_1/^3\xi_2)}{x_1+x_2(^3\xi_1/^3\xi_2)}\right]\left[(1+x_2)\chi^{/}_{12}+2x_1\chi^*\right] \tag{14}$$



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

The unknown χ'_{12} and χ^* parameters of Eq. (14) were evaluated by utilizing measured V^E,κ_S^E, C_P^E and H^E data at two compositions. The calculated parameters were then used to predict the V^E, κ_S^E, C_P^E and H^E values at other values of x_1. Such V^E, κ_S^E, C_P^E, H^E values and $\chi'_{ij}$and χ^* parameters (represented as $\chi_{ij}^{/v}, \chi^{*v}; \chi_{ij}^{/\kappa}, \chi^{*\kappa}; \chi_{ij}^{/C_P}, \chi^{*C_P}; \chi_{ij}^{/H}, \chi^{*H}$) for the investigated mixtures are listed in Tables 7 and 8 respectively. An examination of data in Table 7 indicates that $X^E(X = V or \kappa_S or C_P or H)$ values determined by Graph theory are in agreement with the corresponding experimental data. This provides additional support to the various assumptions made in deriving Eq. (14). Further, comparison of estimated V^E values {via Eq. (14)} with their experimental values support our view point that Eq. (8) was not able to reproduce the V^E values at $x_{IL} > 0.7422$ and 0.5608 for presented mixtures as α_{12} parameter was evaluated by employing V^E value at one composition predict the V^E values of the mixtures changing sign with relative proportion of the constituent molecules.

6. Conclusions

In the present investigations, excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E and excess heat capacities, C_P^E of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (1) + cyclopentanone or cyclohexanone (2) at 293.15, 298.15, 303.15 and 308.15 K with 5 K interval and excess molar enthalpies, H^E of same mixtures at 298.15 K have been measured across full range of composition. The excess properties have been fitted to Redlich-Kister equation to determine adjustable parameters and standard deviations. The connectivity parameters of third degree of a molecule (which in turn depends upon its topology) has been utilized successfully to predict (i) state of components in pure as well as mixed states; (ii) nature and extent of molecular interactions; and (iii) V^E, κ_S^E, C_P^E and H^E values of the mixtures. The analysis of V^E data in terms of Graph theory suggest that (1 + 2) mixtures are characterized by interactions between hydrogen and oxygen atom of cyclopentanone or cyclohexanone with fluorine atom of $[BF_4]^-$ anion and proton of $–CH_3$ groups attached to imidazolium ring of $[Bmmim]^+$ cation. The IR studies also support the presence of molecular entities in the mixtures. The quantum mechanical calculations have also been performed to estimate inter-nuclear distances among the interacting atoms in proposed molecular entities. The analyses of such study also confirm the presence of molecular entities in the mixtures. The V^E, κ_S^E, C_P^E and H^E data have also been analyzed in terms of Graph theory. It has been observed that Graph theory correctly predicts the sign as well as magnitude of V^E, κ_S^E, C_P^E and H^E.

Acknowledgement

The authors are thankful to Mr. K. Chandrasekhar Reddy, SSBN College, Anantapur, for providing Gaussian-09 facility and C-DAC, PUNE, India for providing the computational work.

V. K. Sharma is grateful to University Grant Commission (UGC), New Delhi for the award of SAP.

References

[1] V. Govinda, T. Vasantha, I. Khan, P. Venkatesu, Ind. Eng. Chem. Res. 54 (2015) 9013–9026.
[2] K. Li, T. Kobayashi, Ultrason. Sonochem. 28 (2016) 39–46.
[3] D.W. Fang, W. Guan, J. Tong, Z.W. Wang, J.Z. Yang, J. Phys. Chem. B 112 (2008) 7499–7505.
[4] N. Muhammad, Z.B. Man, M.A. Bustam, M.A. Mutalib, C.D. Wilfred, S. Rafiq, J. Chem. Eng. Data 56 (2011) 3157–3162.
[5] D.M. Fox, J.W. Gilman, H.C. De Long, P.C. Trulove, J. Chem. Thermodyn. 37 (2005) 900–905.
[6] G.R. Sunkara, M.M. Tadavarthi, V.K. Tadekoru, S.K. Tadikonda, S.R. Bezawada, J. Chem. Eng. Data 60 (2015) 886–894.
[7] A. Pal, B. Kumar, T.S. Kang, Fluid Phase Equilib. 358 (2013) 241–249.
[8] X.J. Yan, S.N. Li, Q.G. Zhai, Y.C. Jiang, M.C. Hu, J. Chem. Eng. Data 59 (2014) 1411–1422.
[9] S. Bhagour, S. Solanki, N. Hooda, D. Sharma, V.K. Sharma, J. Chem. Thermodyn. 60 (2013) 76–86.
[10] S. Solanki, N. Hooda, V.K. Sharma, J. Chem. Thermodyn. 56 (2013) 123–135.
[11] H.C. Hua, A.N. Soriano, R.B. Lerona, M.H. Li, Thermochim. Acta 519 (2011) 44–49.
[12] C.H. Li, K.X. Gao, Y.N. Meng, X.K. Wu, F. Zhang, Z.X. Wang, J. Chem. Eng. Data 60 (2015) 1600–1607.
[13] W.Z. Wu, B.X. Han, H.X. Gao, Z.M. Liu, T. Jiang, J. Huang, Angew. Chem. Int. Ed. 43 (2004) 2415–2417.
[14] N. Xing, B. Dai, X. Maa, J. Wei, Y. Pan, W. Guan, J. Chem. Thermodyn. 95 (2016) 21–25.
[15] Y. Xiao, S.V. Malhotra, J. Mol. Catal. A Chem. 230 (2005) 129–133.
[16] Y.O. Andriyko, W. Reischl, G.E. Nauer, J. Chem. Eng. Data 54 (2009) 855–860.
[17] O. Ciocirlan, O. Iulian, J. Chem. Eng. Data 57 (2012) 3142–3148.
[18] G. Chen, Y. Li, W. Zhao, K. Qu, Y. Ning, J. Zhang, Fuel Process. Technol. 133 (2015) 64–68.
[19] D. Dragoescu, J. Mol. Liq. 209 (2015) 713–722.
[20] P.G. Kumari, P. Venkatesu, T. Hofman, M.V.P. Rao, J. Chem. Eng. Data 55 (2010) 69–73.
[21] G. Li, N. Li, X. Wang, X. Sheng, S. Li, A. Wang, Y. Cong, X. Wang, T. Zhang, Energy Fuel 28 (2014) 5112–5118.
[22] H. Jiang, Z. Qu, Y. Li, J. Huang, R. Chen, W. Xing, Chem. Eng. J. 284 (2016) 724–732.
[23] E. Scholz, Karl Fischer Titration, Springer-Verlag, Berlin, 1984.
[24] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents Physical Properties and Methods of Purification, fourth ed. Wiley Interscience, New York, 1986.
[25] G.P. Dubey, M. Sharma, J. Chem. Eng. Data 53 (2008) 1032–1038.
[26] N. Saini, J.S. Yadav, S.K. Jangra, D. Sharma, V.K. Sharma, J. Chem. Thermodyn. 43 (2011) 782–795.
[27] I.B. Malham, M. Turmine, J. Chem. Thermodyn. 40 (2008) 718–723.
[28] V.K. Sharma, J. Kataria, S. Bhagour, J. Therm. Anal. Calorim. 118 (2014) 431–447.
[29] O. Ciocirlan, M. Teodorescu, D. Dragoesce, O. Iulian, A. Barhala, J. Chem. Eng. Data 55 (2010) 3891–3895.
[30] D. Dragoescu, M. Teodorescu, A. Barhala, J. Chem. Thermodyn. 39 (2007) 1452–1457.
[31] M.M. Palaiologou, G.K. Arianas, N.G. Tsierkezos, J. Solut. Chem. 35 (2006) 551–565.
[32] N.A. Lange, Lange's Handbook of Chemistry, 11th ed. Mc Graw-Hill, New York, 1973.
[33] O. Ciocirlan, M. Teodorescu, D. Dragoescu, O. Iulian, A. Barhala, J. Chem. Eng. Data 55 (2010) 968–973.
[34] H.R. Rafiee, S. Ranjbar, F. Poursalman, J. Chem. Thermodyn. 54 (2012) 266–271.
[35] C. Bermudez-Salguero, J. Gracia-Fadrique, E. Calvo, A. Amigo, J. Chem. Eng. Data 56 (2011) 3823–3829.
[36] N.G. Tsierkezos, I.E. Molinou, A.C. Filippou, J. Solut. Chem. 34 (2005) 1371–1386.
[37] V.K. Sharma, A. Rohilla, Thermochim. Acta 568 (2013) 140–147.
[38] V.K. Sharma, S. Solanki, S. Bhagour, D. Sharma, Thermochim. Acta 569 (2013) 36–41.
[39] R. Sabbah, A. Xu-Wu, J.S. Chickos, M.L.P. Leitao, M.V. Roux, L.A. Torres, Thermochim. Acta 331 (1999) 93–204.
[40] R. Fuchs, Can. J. Chem. 58 (1980) 2305–2306.
[41] K. Nishikawa, K. Ohomura, K. Tamura, S. Murakami, Thermochim. Acta 267 (1995) 323–332.
[42] G.C. Benson, O. Kiyohara, J. Chem. Thermodyn. 11 (1979) 1061–1064.
[43] P. Brocos, A. Amigo, M. Points, E. Calvo, R. Bravo, Thermochim. Acta 286 (1996) 297–306.
[44] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345–348.
[45] H. Gupta, J. Kataria, D. Sharma, V.K. Sharma, J. Chem. Thermodyn. 103 (2016) 189–205.
[46] H. Gupta, S. Solanki, V.K. Sharma, J. Therm. Anal. Calorim. (2016)http://dx.doi.org/10.1007/s10973-016-5820-0.
[47] J. Jadzyn, J. Swiergiel, J. Chem. Eng. Data 56 (2011) 4715–4719.
[48] S.K. Neeti, J.S. Jangra, Dimple Yadav, V.K. Sharma, J. Mol. Liq. 163 (2011) 36–45.
[49] V.K. Sharma, S. Kumar Romi, Thermochim. Acta 417 (2004) 91–97.
[50] V.K. Sharma, S. Kumar, Thermochim. Acta 413 (2004) 255–259.
[51] V.K. Sharma, J. Kataria, S. Solanki, J. Solut. Chem. 43 (2014) 486–524.
[52] L.B. Kier, S.H. Yalkowasky, A.A. Sinkula, S.C. Valvani, Physicochemical Properties of Drugs, Chapter 9, Mercel Dekker, New York, 1980 282–295.
[53] C.N.R. Rao, Chemical Application of Infrared Spectroscopy, Academic Press, London, 1963.
[54] Y. Andriyko, A. Andriiko, O.B. Babushkina, G.E. Nauer, Electrochim. Acta 55 (2010) 1081–1089.
[55] Z. Samadi, M. Mirzaei, N.L. Hadipour, S.A. Khorami, J. Mol. Graph. Model. 26 (2008) 977–981.
[56] B. Yogeswari, R. Kanakaraju, S. Boopathi, P. Kolandaivel, J. Mol. Graph. Model. 35 (2012) 11–20.
[57] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
[58] M.C. Sekhar, A. Venkatesulu, T.M. Mohan, M. Gowrisankar, Orient. J. Chem. 31 (2015) 897–906.
[59] M.R. Housaindokht, H.E. Hosseini, M.S.S. Googheri, H. Monhemi, R.I. Najafabadi, N. Ashraf, M. Gholizadeh, J. Mol. Liq. 177 (2013) 94–101.
[60] M.L. Huggins, J. Phys. Chem. 74 (1970) 371–378.
[61] M.L. Huggins, Polymer 12 (1971) 389–399.
[62] P.P. Singh, M. Bhatia, J. Chem. Soc. Faraday Trans. 1 (85) (1989) 3807–3812.