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Molar heat capacity of four aqueous ionic liquid mixtures

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ABSTRACT

As a continuation of our systematic study on physicochemical characterization of aqueous solution of ionic liquids, new measurements of molar heat capacity for aqueous solutions of four ionic liquids were reported. The investigated ionic liquids were 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate. The molar heat capacities were measured at standard pressure and over the temperature range (303.2–353.2) K using a differential scanning calorimeter (DSC) having an estimated experimental uncertainty of about ±2% with liquid water as reference. The measured molar heat capacities were reported as function of temperature and composition and the excess molar heat capacities were calculated using a Redlich–Kister type equation. For the studied ionic liquids, results showed variations in the dependence of the excess molar heat capacities on temperature and composition. The applied correlation satisfactorily represented the molar heat capacity measurements as shown by an acceptable overall average deviation of 0.09%.

1. Introduction

Room-temperature ionic liquids (RTILs) are regarded to as promising green alternatives to volatile organic solvents. They are organic salts that consist entirely of ions and liquid at or below room temperature. They posses unique properties, including wide liquid range, extremely low vapor pressure, high thermal stability, high solvation capacity, and non-flammability, which suggest their possible applications in a wide variety of industrial and chemical processes [1]. Several studies reported that RTILs have the potential as absorption media in CO_2 capture, as working fluids in electrochemical processes (i.e., batteries, capacitors, etc.), and as heat-transfer or thermal fluids [2–6] and the use of their aqueous mixtures in such applications maybe inevitable [7].

The suitability of RTILs for use as working fluids for a specific process depends greatly on their physical and thermodynamic properties. These parameters will be vital in the process design. For heat-transfer applications, for instance, one of the relevant properties is the heat capacity. This property indicates the ability of the substance to store heat; thus, it can be used to assess the efficacy of the substance as a thermal fluid. Several papers reported heat capacity data for a number of pure RTILs for a variety of temperature ranges [1,2,4,8–13] while only few reported those of aqueous RTIL solutions. On the latter, available data are for water + RTIL solutions of 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylpyridinium tetrafluoroborate, 1-*n*-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazoliumtosylate, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium ethylsulfate, 1-ethyl-3-methylimidazoliummethylsufate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (or triflate), 1-ethyl-3-methylimidazolium trifluoroacetate, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate [7,8,10,14–18]. In fact of the four studied systems in this work, only that of 1-butyl-3-methylimidazolium bromide + water systems are available [10].

Thus, in this work, the molar heat capacities, C_P, of aqueous mixtures of the RTILs 1-butyl-3-methylimidazolium chloride [Bmim][Cl], 1-butyl-3-methylimidazolium bromide [Bmim][Br], 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [Bdmim][BF_4], and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [Bdmim][PF_6] were determined at standard pressure, within the temperature range (303.15–353.15) K and over the entire range of mole fraction depending on the solubility of the RTIL in water. Also the excess molar heat capacity, C_P^E, was calculated using a Redlich–Kister type equation and the dependences of the measured C_P and calculated C_P^E on system's temperature and composition were presented.

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Table 1
Ionic liquids investigated in this study and their melting points.

Ionic liquid	Abbreviation	Melting point (°C)[a]
1-Butyl-3-methylimidazolium chloride	[Bmim][Cl]	57
1-Butyl-3-methylimidazolium bromide	[Bmim][Br]	73
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	[Bdmim][BF_4]	32
1-Butyl-2,3-dimethylimidazolium hexafluorophosphate	[Bdmim][PF_6]	38

[a] The values are as reported by the supplier and were measured before the samples' purification.

Table 2
Molar heat capacities of [Bmim][Cl] (1) + H_2O (2) solutions.

T/K	Molar heat capacity, C_P/(J mol^{-1} K^{-1}) $x_1 = 0.20$	$x_1 = 0.40$	$x_1 = 0.60$	$x_1 = 0.80$
303.2	125.6 ± 1.2[a]	170.2 ± 0.7	218.6 ± 0.2	272.6 ± 3.6
308.2	126.7 ± 1.2	171.6 ± 0.5	220.0 ± 0.2	274.4 ± 3.7
313.2	127.7 ± 1.2	173.0 ± 0.5	221.8 ± 0.2	276.3 ± 3.5
318.2	128.6 ± 1.1	174.5 ± 0.7	223.9 ± 0.3	279.3 ± 3.5
323.2	129.9 ± 1.1	176.2 ± 0.5	225.9 ± 0.7	280.9 ± 3.5
328.2	130.9 ± 1.1	177.6 ± 0.5	228.0 ± 0.4	282.9 ± 3.7
333.2	131.8 ± 0.9	179.0 ± 0.5	230.0 ± 0.3	285.5 ± 3.3
338.2	133.1 ± 1.0	180.5 ± 0.5	232.0 ± 0.2	288.2 ± 3.6
343.2	133.8 ± 0.9	182.2 ± 0.1	234.1 ± 0.2	290.5 ± 3.5
348.2	135.2 ± 0.9	183.6 ± 0.7	236.4 ± 0.6	293.1 ± 3.4
353.2	136.0 ± 0.9	185.9 ± 1.0	238.6 ± 0.4	296.3 ± 3.4

[a] Mean standard deviation.

2. Experimental

2.1. Chemicals

The RTILs used in this work, i.e. 1-butyl-3-methylimidazolium chloride (purity ≥ 99%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (purity ≥ 99%), 1-butyl-3-methylimidazolium bromide (purity ≥ 98%), and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate (purity ≥ 97%), were purchased, respectively, from Alfa Aesar, ACROS, and Fluka. Each sample was vacuum dried for a minimum of 4 days to remove any volatile impurities and the water content was measured using a Mettler Toledo Karl-Fischer titrator (model DL31). The water content of each sample after drying was found to be ≤ 0.005 (mass fraction). Type I reagent grade deionized water with resistivity of 18.3 MΩ cm, processed in a Barnstead Thermolyne ultrapure water system (model EasyPure 1052), was used to calibrate the DSC and to prepare the aqueous solutions. All weight measurements were performed on a Mettler Toledo digital balance (model AL204) with an accuracy of $\pm 1 \times 10^{-4}$ g.

All RTILs used were solid at room temperature (see melting point values in Table 1). Among the four, only two systems were found to be totally soluble in water, i.e. [Bmim][Cl] and [Bdmim][BF_4]. Therefore, for the binary systems of [Bmim][Cl] (1) + H_2O (2) and [Bdmim][BF_4] (1) + H_2O (2) solutions were prepared at ($x_1 = 0.20$, 0.40, 0.60, and 0.80) while for [Bmim][Br] (1) + H_2O (2) and [Bdmim][PF_6] (1) + H_2O (2), the mole fractions ($x_1 = 0.10$, 0.20, 0.30, 0.40, 0.50, and 0.60) and ($x_1 = 0.80$, 0.85, 0.90, and 0.95) were considered, respectively.

2.2. Measurement of molar heat capacity

The C_P was measured using a differential scanning calorimeter (Model DSC-2010) equipped with a thermal analysis controller from TA Instruments. The apparatus and the experimental procedures were described in the previous work of Chiu et al. [19] and some pertinent details are repeated in the succeeding paragraphs.

By creating a baseline profile, a standard sample profile, and a sample profile, the specific heat of a substance can be determined conveniently and rapidly with a DSC. The thermograms were plotted via the data analysis program and the specific heat of the considered sample was determined by measuring the difference in y-axis displacement (calorimetric differential) between the sample and blank curves at any desired temperature. The specific heat of the sample, $\overline{C_P}$, in J g^{-1} K^{-1} was calculated using the equation

$$\overline{C_P} = \left[\frac{60E}{H_r}\right]\frac{\Delta H}{m} \tag{1}$$

where E is the cell calibration coefficient at the systems' temperature, H_r the heating rate (K min^{-1}), ΔH the difference in y-axis deflection between sample and blank curves at the systems' temperature (mW), and m the sample mass (mg). In Eq. (1), the quantity ($60\,E/H_r$) is a constant under a given set of experimental conditions. This quantity converts the measurement directly into units of specific heat of J g^{-1} K^{-1}. The value of ($60\,E/H_r$) was determined by running a standard sapphire (Al_2O_3) under conditions identical to those of the unknown sample. Then the obtained values of ΔH, m, and $\overline{C_P}$ of the standard sapphire were substituted into Eq. (1) at the temperature of interest. During the run, a method was created that holds isothermally at the desired starting temperature (25 °C) for 10 min, heats at the set heating rate, and then holds at the temperature limit (82 °C) for 10 min.

The uncertainty of the C_P measurements was estimated to be ±2% with liquid water as reference. The details of the calibration (validation) procedures for the C_P measurements were discussed in our previous works [13,14]. All measurements were carried out in three to five replicate runs and the mean (average) values were reported.

3. Results and discussion

The molar heat capacities, C_P, for the aqueous binary solutions of [Bmim][Cl], [Bmim][Br], [Bdmim][BF_4], and [Bdmim][PF_6] were measured over the temperature range (303.2–353.2) K and standard pressure. The obtained C_P values and the corresponding mean standard deviations are tabulated in Tables 2–5. The temperature- and composition dependence of the obtained C_P data were representatively discussed using the binary solutions of [Bmim][Cl] which are plotted in Fig. 1. Results show that for the aqueous systems, C_P values increase slightly with temperature for high-RTIL content solutions and the effect decreases for high-water content solutions. It is also clearly shown that the C_P of pure [Bmim][Cl] is much higher than that of pure water. These are due to the dependence of C_P on the number of translational, vibrational, and rotational energy storage modes in the molecule and the high molecular weight of the RTIL compared to that of water [7,20]. As expected, the C_P of the aqueous solutions of the RTILs increases with increasing RTIL mole fraction in the mixture. The same have been observed for the other RTIL systems investigated in this study. These trends also agree with those reported in the literature [7,8] and in our previous works [9,12–14,18].

For the considered binaries, only very few (inconsistent) data are available for the C_P of the corresponding pure RTILs; thus, the latter were also measured in this study. Table 6 shows the obtained C_P data for the pure RTIL systems. As shown in this table, for each system C_P was measured over different ranges of temperature. Due to the difference in their melting points (as shown in Table 1), the temperature range at which the RTILs exist as liquid varies. In this work, measurements were done only at temperature conditions at which the RTILs were in the liquid state.

For the purpose of evaluating the molar heat capacity of the pure RTIL systems, the present C_P data were correlated as function

Table 3
Molar heat capacities of [Bmim][Br] (1) + H_2O (2) solutions.

T/K	Molar heat capacity, C_P/(J mol^{-1} K^{-1}) $x_1 = 0.10$	$x_1 = 0.20$	$x_1 = 0.30$	$x_1 = 0.40$	$x_1 = 0.50$	$x_1 = 0.60$
303.2	102.2 ± 0.9	123.4 ± 3.3	144.5 ± 1.1	165.0 ± 1.3	186.7 ± 3.8	209.6 ± 1.4
308.2	102.5 ± 1.0	124.1 ± 3.1	145.4 ± 1.2	166.1 ± 1.3	188.0 ± 3.6	211.2 ± 1.4
313.2	103.0 ± 0.9	124.9 ± 2.9	146.3 ± 1.0	167.1 ± 1.3	189.2 ± 3.6	212.9 ± 1.5
318.2	103.5 ± 0.8	125.8 ± 2.9	147.2 ± 1.1	168.1 ± 1.2	190.7 ± 3.6	214.5 ± 1.6
323.2	104.0 ± 0.9	126.6 ± 2.8	148.2 ± 0.8	169.2 ± 1.2	191.8 ± 3.3	216.2 ± 1.6
328.2	104.5 ± 0.8	127.5 ± 2.6	149.2 ± 0.8	170.4 ± 1.2	193.3 ± 3.3	217.9 ± 1.6
333.2	104.8 ± 0.9	128.3 ± 2.5	150.1 ± 0.9	171.6 ± 1.2	194.6 ± 3.3	219.5 ± 1.6
338.2	105.4 ± 0.8	129.2 ± 2.3	151.1 ± 0.8	172.9 ± 1.2	196.1 ± 3.1	221.3 ± 1.7
343.2	105.8 ± 1.0	130.0 ± 2.0	152.1 ± 0.7	173.9 ± 1.1	197.3 ± 3.1	223.1 ± 1.9
348.2	106.3 ± 0.8	131.1 ± 1.9	153.1 ± 0.6	175.2 ± 1.2	198.6 ± 3.2	224.9 ± 1.7
353.2	106.8 ± 0.8	131.9 ± 1.8	154.1 ± 0.8	176.2 ± 1.2	200.0 ± 3.1	226.5 ± 1.9

Table 4
Molar heat capacities of [Bdmim][BF_4] (1) + H_2O (2) solutions.

T/K	Molar heat capacity, C_P/(J mol^{-1} K^{-1}) $x_1 = 0.20$	$x_1 = 0.40$	$x_1 = 0.60$	$x_1 = 0.80$
303.2	146.9 ± 2.2	217.5 ± 1.6	284.4 ± 1.0	343.0 ± 3.4
308.2	147.2 ± 2.2	218.2 ± 1.6	285.6 ± 1.0	344.2 ± 3.7
313.2	147.8 ± 2.4	219.3 ± 1.6	287.0 ± 1.4	346.3 ± 3.6
318.2	148.4 ± 2.3	220.4 ± 1.6	288.6 ± 1.3	348.5 ± 3.5
323.2	149.1 ± 2.4	221.7 ± 1.5	290.3 ± 1.4	351.0 ± 3.4
328.2	149.8 ± 2.4	223.2 ± 1.4	292.1 ± 1.8	353.2 ± 3.3
333.2	150.4 ± 2.4	224.1 ± 1.4	293.5 ± 2.2	355.6 ± 3.6
338.2	151.1 ± 2.5	225.2 ± 1.5	295.7 ± 2.1	358.1 ± 3.7
343.2	151.7 ± 2.4	226.4 ± 1.3	297.6 ± 2.3	360.8 ± 3.4
348.2	152.4 ± 2.7	227.7 ± 1.4	299.5 ± 2.6	363.5 ± 3.2
353.2	153.1 ± 2.6	229.2 ± 1.4	301.7 ± 2.6	366.3 ± 3.1

Table 5
Molar heat capacities of [Bdmim][PF_6] (1) + H_2O (2) solutions.

T/K	Molar heat capacity, C_P/(J mol^{-1} K^{-1}) $x_1 = 0.80$	$x_1 = 0.85$	$x_1 = 0.90$	$x_1 = 0.95$
303.2	387.0 ± 2.3	396.4 ± 0.8	407.2 ± 3.1	418.3 ± 2.8
308.2	389.2 ± 2.7	398.4 ± 0.9	409.4 ± 3.4	420.5 ± 3.1
313.2	391.2 ± 2.7	400.5 ± 0.6	411.9 ± 3.7	423.3 ± 3.6
318.2	393.4 ± 3.3	402.7 ± 0.7	414.5 ± 3.5	426.0 ± 3.5
323.2	395.9 ± 3.6	405.5 ± 0.9	417.7 ± 3.8	429.4 ± 4.0
328.2	398.9 ± 3.7	408.8 ± 0.7	421.3 ± 3.5	433.2 ± 3.9
333.2	401.8 ± 3.6	411.9 ± 0.8	424.7 ± 3.7	436.7 ± 3.5
338.2	404.5 ± 3.9	414.9 ± 0.4	428.0 ± 3.4	440.1 ± 3.1
343.2	407.5 ± 3.6	417.9 ± 0.8	431.2 ± 3.0	443.5 ± 2.7
348.2	411.1 ± 3.8	421.7 ± 0.7	435.2 ± 3.0	447.6 ± 2.7
353.2	414.1 ± 3.6	424.8 ± 0.6	438.3 ± 3.0	450.9 ± 2.6

Table 6
Molar heat capacities of pure systems considered in this work.

T/K	molar heat capacity, $C_{P,i}$/(J mol^{-1} K^{-1}) [Bmim][Cl]	[Bmim][Br]	[Bdmim][BF_4]	[Bdmim][PF_6]
313.2			397.3 ± 2.8	
318.2			398.8 ± 2.7	
323.2			400.6 ± 2.3	439.3 ± 1.3
328.2			403.3 ± 2.5	442.9 ± 1.3
333.2			405.4 ± 2.9	446.2 ± 1.1
338.2			407.8 ± 3.0	449.4 ± 1.3
343.2	337.2 ± 3.6		410.6 ± 2.9	452.7 ± 1.3
348.2	340.3 ± 3.4		413.5 ± 3.2	457.0 ± 1.3
353.2	343.3 ± 3.3	334.8 ± 2.5	416.5 ± 3.2	460.1 ± 0.9
358.2	347.1 ± 3.2	338.1 ± 2.8	420.2 ± 3.5	464.4 ± 1.0
363.2	350.6 ± 2.7	341.1 ± 2.7	423.6 ± 3.4	468.0 ± 1.0
368.2	354.3 ± 2.8	344.6 ± 3.1	427.3 ± 3.9	471.6 ± 1.5
373.2	357.6 ± 2.4	347.5 ± 3.0	430.6 ± 3.8	475.1 ± 1.3
378.2	361.0 ± 2.5	350.6 ± 3.4	434.4 ± 4.1	478.9 ± 1.2
383.2	364.3 ± 2.7	354.1 ± 3.3	436.3 ± 2.8	482.6 ± 1.6
388.2	367.4 ± 2.6	356.7 ± 3.7		
393.2	370.7 ± 2.8	359.9 ± 3.9		
398.2	374.0 ± 2.9	363.4 ± 3.9		
403.2	376.8 ± 2.3	366.4 ± 3.8		

of temperature using the empirical equation of the form

$$C_P/\mathrm{J} \times \mathrm{mol}^{-1} \times \mathrm{K}^{-1} = a_0 + a_1(T/\mathrm{K}) + a_2(T/\mathrm{K})^2 \qquad (2)$$

where a_i are empirical constants which are determined by fitting the present C_P data of the pure RTILs using Eq. (2). The determined empirical constants and the corresponding absolute average deviation (AAD) for the pure RTILs investigated are presented in Table 7. Based on the overall AAD% of 0.06 for a total of 52 data points, it can be said that the obtained constants for Eq. (2) successfully correlated the C_P of the pure RTILs with temperature.

The excess molar heat capacity, C_P^E, is the difference between the heat capacity of the mixture and the summation of the pure components contribution and was calculated using the expression cited in the work of Lide and Kehiaian [21] which is as follows:

$$C_P^E = C_P - \sum_i x_i C_{P,\,i} \qquad (3)$$

where $C_{P,i}$ is the molar heat capacity of the pure system. For liquid water, the C_P data by Osborne et al. [22] was used while for the pure RTIL, the calculated values from Eq. (2) were used.

The excess molar heat capacities, C_P^E, obtained in this work are shown in Figs. 2–5. As depicted in Fig. 2, the C_P^E for [Bmim][Cl] + H_2O mixtures have both positive and negative values with maxima

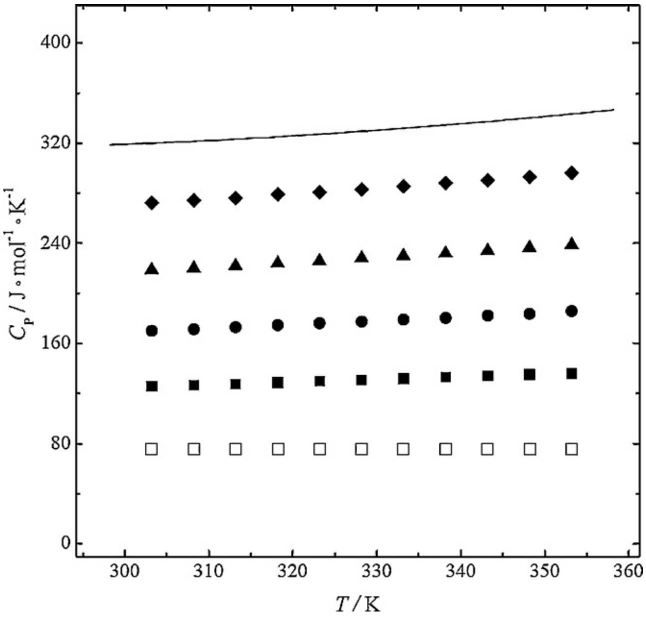

Fig. 1. Plot of molar heat capacity against temperature for [Bmim][Cl] (1) + H_2O (2) solution at different mole fractions: ■, $x_1 = 0.2$; ●, $x_1 = 0.4$; ▲ $x_1 = 0.6$; ◆, $x_1 = 0.8$, data from this work; □, liquid water, data from Osborne et al. [22]; and line, pure [Bmim][Cl], calculated using Eq. (2).

Table 7
Constants of Eq. (3)[a] for the considered pure ionic liquid systems.

System	Constants			No. of data points, n	AAD[b]/%
	a_0	a_1	a_2		
[Bmim][Cl]	12.850	1.1768	-6.7752×10^{-4}	13	0.05
[Bmim][Br]	93.769	0.72899	-1.3039×10^{-4}	11	0.04
[Bdmim][BF_4]	549.80	−1.3658	2.8015×10^{-3}	15	0.10
[Bdmim][PF_6]	279.54	0.2989	6.0488×10^{-4}	13	0.05
	overall	52	0.06		

[a] $C_P/\text{J} \times \text{mol}^{-1} \times \text{K}^{-1} = a_0 + a_1(T/\text{K}) + a_2(T/\text{K})^2$

[b] $AAD/\% = \frac{100}{n} \times \sum_{i=1}^{n} \left| (\varepsilon_{\text{cald}} - \varepsilon_{\text{expt}})/\varepsilon_{\text{expt}} \right|_i$, where $\varepsilon_{\text{cald}}$ and $\varepsilon_{\text{expt}}$ correspond to calculated and experimental values, respectively

Table 8
Parameters of Eq. (4)[a] for the considered aqueous ionic liquid systems.

System	i	Parameters		No. of data points	AAD/%	
		$b_{i,0}$	$b_{i,1}$		C_P	C_P^E
[Bmim][Cl] + H_2O	1	−161.53	0.48237	44	0.1	
	2	15.944	−0.05411	44	0.1	12.4
	3	−63.993	0.45373			
[Bmim][Br] + H_2O	1	56.114	−0.21479			
	2	55.476	−0.20389	66	0.1	5.6
	3	−141.03	0.69529			
[Bdmim][BF_4] + H_2O	1	−9.7013	0.26468			
	2	−102.25	0.43097	44	0.1	1.5
	3	−207.94	0.65014			
[Bdmim][PF_6] + H_2O	1	−1549.4	6.7117			
	2	5526.7	−20.778	44	0.04	1.2
	3	−4641.6	16.742			
			Overall	198	0.09	5.2

[a] $C_P^E/\text{J} \times \text{mol}^{-1} \times \text{K}^{-1} = x_1 x_2 \sum_{i=1}^{n} B_i (x_1 - x_2)^{i-1}$ where $B_i = b_{i,0} + b_{i,1}(T/\text{K})$.

at low and high RTIL mole fractions and a minimum at intermediate composition and a positive temperature dependence. For [Bmim][Br] + H_2O mixtures (Fig. 3) positive C_P^E values are observed at low RTIL mole fractions that changes into inflexions (at $x_1 \sim 0.3$) and reaches a minimum (negative) at intermediate composition ($x_1 \sim 0.5$). It can also be observed that at the lower composition the C_P^E values increase with increasing temperature while at the higher composition they decrease with increasing temperature. This trend is similar to that observed in our previous work on aqueous systems of [Emim][C_2N_3] [18]. For both [Bmim][Cl] + H_2O and [Bmim][Br] + H_2O, the negative values of the C_P^E are probably due to the presence of RTIL/water interactions which are stronger than

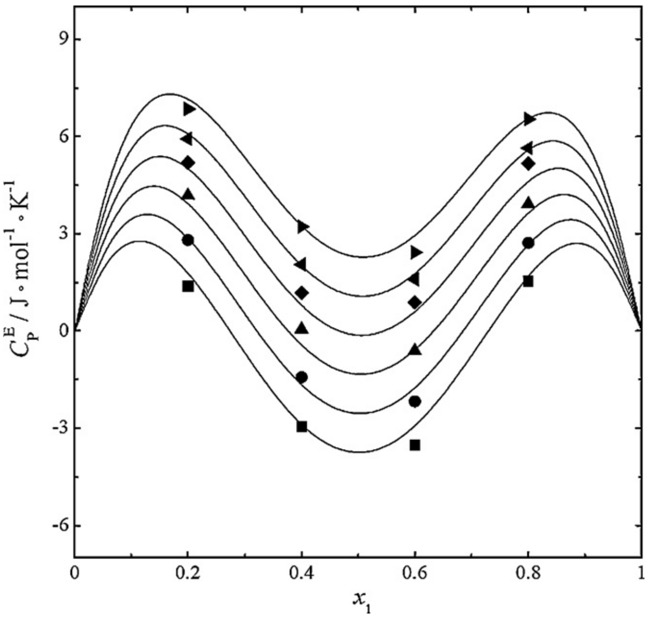

Fig. 2. Plot of excess molar heat capacity against x_1 for [Bmim][Cl] (1) + H_2O (2) solution at different temperatures: ■, 303.2 K; ●, 313.2 K; ▲, 323.2 K; ♦, 333.2 K; ◄, 343.2 K; ►, 353.2 K; and lines, calculated using Eq. (4).

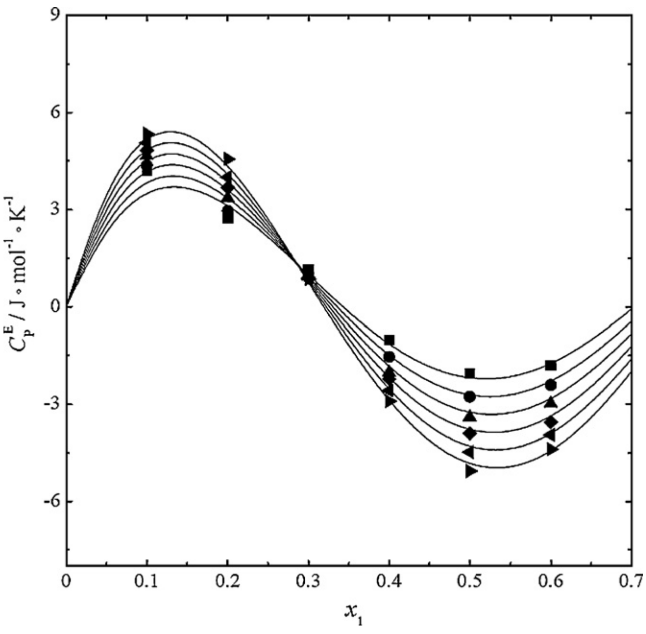

Fig. 3. Plot of excess molar heat capacity against x_1 for [Bmim][Br] (1) + H_2O (2) solution at different temperatures: ■, 303.2 K; ●, 313.2 K; ▲, 323.2 K; ♦, 333.2 K; ◄, 343.2 K; ►, 353.2 K; and lines, calculated using Eq. (4).

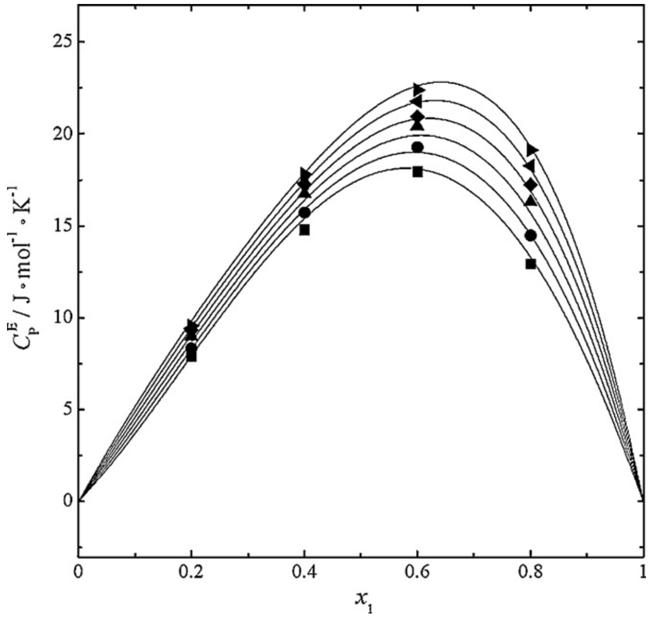

Fig. 4. Plot of excess molar heat capacity against x_1 for [Bdmim][BF$_4$] (1) + H_2O (2) solution at different temperatures: ■, 303.2 K; ●, 313.2 K; ▲, 323.2 K; ♦, 333.2 K; ◄, 343.2 K; ►, 353.2 K; and lines, calculated using Eq. (4).

the corresponding RTIL/RTIL and water/water interactions in the aqueous mixtures while the positive values suggest otherwise. For [Bdmim][BF$_4$] + H_2O mixtures (Fig. 4), positive C_P^E were obtained over the complete composition range reaching a maximum at intermediate composition ($x_1 \sim 0.6$) and with positive temperature dependence. The C_P^E values for the [Bdmim][PF$_6$] + H_2O mixtures are also positive over the entire composition range considered but the trend in the temperature is that the C_P^E decreases with increasing RTIL mole fraction. It can also be noted that more positive and higher C_P^E values were obtained for the [Bdmim]-based systems relative to the [Bmim]-based systems studied which maybe indicative of weaker RTIL/water interactions in the former.

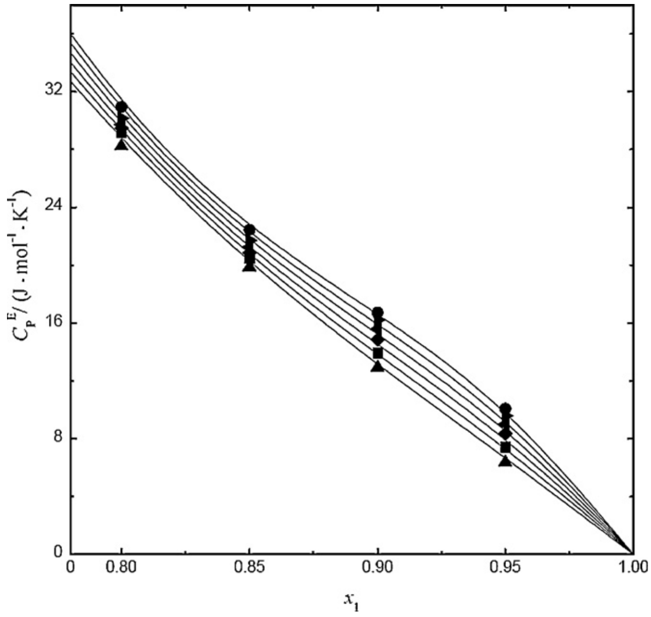

Fig. 5. Plot of excess molar heat capacity against x_1 for [Bdmim][PF$_6$] (1) + H_2O (2) solution at different temperatures: ■, 303.2 K; ●, 313.2 K; ▲, 323.2 K; ♦, 333.2 K; ◄, 343.2 K; ►, 353.2 K; and lines, calculated using Eq. (4).

For application and generalization purposes, the temperature and composition dependences of C_P^E were correlated using a Redlich–Kister type equation of the form

$$C_P^E/\text{J} \times \text{mol}^{-1} \times \text{K}^{-1} = x_1 x_2 \sum_{i=1}^{n} B_i (x_1 - x_2)^{i-1} \tag{4}$$

where B_i was assumed to follow the equation

$$B_i = b_{i,0} + b_{i,1}(T/\text{K}) \tag{5}$$

The parameters $b_{i,0}$ and $b_{i,1}$ for the studied binaries were determined by fitting the C_P data from this work using Eq. (4) and the results are presented in Table 8. The number of terms (B_i), in Eq. (4), which should be used to represent C_P^E, depends on the degree of complexity of the binary systems. Here, three terms in Eq. (4) were found to satisfactory correlate the present measurements as indicated by a reasonable overall AAD of 0.09 and 5.2% for C_P and C_P^E, respectively, for a total of 198 data points. Eq. (4) successfully represented the temperature and composition dependence of the excess molar heat capacity of the studied solvent systems, as seen in Figs. 2–5 via the smoothed curves.

4. Conclusions

The molar heat capacities were measured for aqueous solutions of [Bmim][Cl], [Bmim][Br], [Bdmim][BF$_4$], and [Bdmim][PF$_6$] over a complete range of composition and for temperatures (303.2–353.2) K. The measured values were presented as functions of temperature and composition of the solvent system. The C_P of the pure RTILs varied slightly (linearly) with temperature at high RTIL concentrations. The derived correlation successfully represented the variation of C_P as indicated by the overall AAD% of 0.06. For the aqueous solutions, the C_P increased with increasing RTIL mole fraction in the mixture. The excess molar heat capacity expression in the form of a Redlich–Kister type equation satisfactorily correlated the dependence of the C_P on temperature and composition owing to the values of AAD% of 0.09 for C_P and 5.2 for C_P^E. It can be concluded, therefore, that the present data were successfully represented by the applied correlations; thus, they are of sufficient accuracy for engineering design calculations.

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