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Molar heat capacity and electrolytic conductivity of aqueous solutions of [Bmim][$MeSO_4$] and [Bmim][triflate]

Pei-Yin Lin[a], Allan N. Soriano[a], Alvin R. Caparanga[a,b], Meng-Hui Li[a,*]

[a] *R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chung Li 32023, Taiwan*
[b] *School of Chemical Engineering and Chemistry, Mapúa Institute of Technology, Manila 1002, Philippines*

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ABSTRACT

Here we report the new measurements of molar heat capacity, C_P and electrolytic conductivity, σ for aqueous solutions of 1-butyl-3-methylimidazolium methylsulfate, [Bmim][$MeSO_4$] and 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [Bmim][triflate]. Heat capacities were measured from 303.2 to 353.2 K with a differential scanning calorimeter. Electrolytic conductivities were measured from 293.2 to 353.2 K with a commercial conductivity meter. The estimated uncertainties of C_P and σ measurements were ±2 and ±1%, respectively. The present measurements of C_P and σ were presented as a function of temperature and composition. An excess molar heat capacity C_P^E expression using the Redlich–Kister equation for the temperature and composition dependence was used to represent the measured C_P and a modified empirical equation was used to correlate the temperature and composition dependence of the measured σ of the studied systems. The applied correlations represent the C_P and σ measurements satisfactorily. The C_P and σ values presented in this work are, in general, of sufficient accuracy for most engineering-design calculations.

1. Introduction

Ionic liquids (ILs), a new class of environmentally benign substance, have been considered by many studies to be alternative solvents to aqueous alkanolamines for reduction or removal of acid gas impurities, CO_2 and H_2S, from natural and refinery gas streams by absorption [1–8]. ILs, which are usually molten salts and liquid at room temperature, have appealing physical properties such as low vapor pressure, non-flammability, high thermal stability and high solvation capacity making it an ideal candidate to replace conventional solvents not only in gas treatment but also in other industrial chemical processes.

The data bank for properties of ILs, e.g., molar heat capacity, C_P and electrolytic conductivity, σ, is still wanting. Many studies have reported heat capacities and electrolytic conductivities of pure ILs; however, those for mixtures containing ILs are scant. Heat capacities of the following systems have been reported: binary mixture of 1-butyl-3-methylpyridinium tetrafluoroborate and a molecular solvent (ethanol, nitromethane and water) [9], aqueous 1-n-butyl-3-methylimidazolium bromide [10], aqueous 1-n-butyl-3-methylimidazolium tosylate [11], and aqueous 1-n-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate [12] systems. Recent work of Garcia-Miaja et al. [13] presented new results of heat capacity for [Bmim][$MeSO_4$] and [Bmim][triflate] but only at 303.15 K. Reports on electrolytic conductivities of mixtures involving ILs are also few. Some of these would be for systems such as binary mixtures of an IL and a molecular liquid [14], binary mixtures of an IL and an aluminum halide [15], and binary mixtures of an IL and an alcohol (ethanol) or a ketone (acetone) [16]. There are only a few other reports on electrolytic conductivities of aqueous solutions of ILs [4,12,15–19], none of these investigated the considered systems: [Bmim][$MeSO_4$] and [Bmim][triflate].

Thus, in this work, heat capacities and electrolytic conductivities of aqueous solutions of [Bmim][$MeSO_4$] and [Bmim][triflate] were investigated for wider temperature range. The studied systems were noted as [Bmim][$MeSO_4$] + H_2O and [Bmim][triflate] + H_2O throughout the text. Heat capacities were measured from 303.2 to 353.2 K at normal atmospheric condition with a differential scanning calorimeter (DSC) and the electrolytic conductivities were measured from 293.2 to 353.2 K at normal atmospheric condition with a commercial conductivity meter. Both physical properties were presented and correlated as a function of temperature and composition. An excess molar heat capacity C_P^E expression using the Redlich–Kister equation for the temperature and composition dependence was used to represent the measured C_P of the studied systems. An empirical equation proposed in previous work of Graber et al. [20] was modified to express the correlation of the measured σ as a function of temperature and composition.

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[*] Corresponding author. Tel.: +886 3 265 4109; fax: +886 3 265 4199.
E-mail address: mhli@cycu.edu.tw (M.-H. Li).

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2. Experimental

2.1. Chemicals

The IL samples, [Bmim][MeSO$_4$] and [Bmim][triflate], were purchased from Strem Co. and TCI Co., respectively. The minimum purity (in mass fraction) and the water content (in mass fraction) of the IL samples were ($\geq$0.980 and $\geq$0.981) and ($\leq$0.009 and $\leq$0.007), for [Bmim][MeSO$_4$] and [Bmim][triflate], respectively. The samples were used without further purification, i.e., further reduction of water content, since it would be mixed with water later to form aqueous solutions. The water used to prepare the aqueous solutions was processed in Barnstead Thermodyne (model Easy Pure 1052) to produce deionized water with a resistivity of 18.3 MΩ cm and TOC (total organic content) of less than 15 ppb. All weight measurements during the preparation of solutions were performed on digital balance having $\pm 1 \times 10^{-4}$ g accuracy. A standard KCl solution (0.1N) was used to calibrate the conductivity meter (Merck).

2.2. Measurements of heat capacity and electrolytic conductivity

The apparatus (including its specifications) and the experimental procedures for the C_P and σ measurements were the same as those described by Chiu et al. [21] and Yu et al. [22], respectively. Therefore, only the frequency and the uncertainty of the measurements were mentioned here. For more details, the reader is referred to the above mentioned papers [21,22].

The C_P and σ measurements were carried out in three to five replicate runs and the average value was reported. On the basis of comparison with literature values for water, the uncertainty of the C_P measurements is estimated to be ±2%. The uncertainty of the σ measurements using the conductivity meter was estimated to be ±1% with the calibrating solution as the reference.

3. Results and discussion

3.1. Heat capacity

To validate the applied apparatus and experimental procedure for C_P measurements, the values of C_P of pure [Bmim][triflate] has been measured for temperatures from 303.2 to 353.2 K. Fig. 1 shows the comparison of the C_P data for pure [Bmim][triflate] between this work and the available literature values. As shown in Fig. 1, the measured C_P data for the pure [Bmim][triflate] were very consistent with the C_P data of Diedrichs and Gmehling [6] and that of Yu et al. [22] while the C_P value of Fredlake et al. [1] appeared to be lower than all the reported values in the literature and from this work. The present C_P data were in general, of good agreement with most of the available literature values, thus validating the applied apparatus and experimental procedure for the C_P measurements. The C_P data of pure [Bmim][triflate] from this work along with the consistent literature data were then correlated as a function of temperature via Eq. (1).

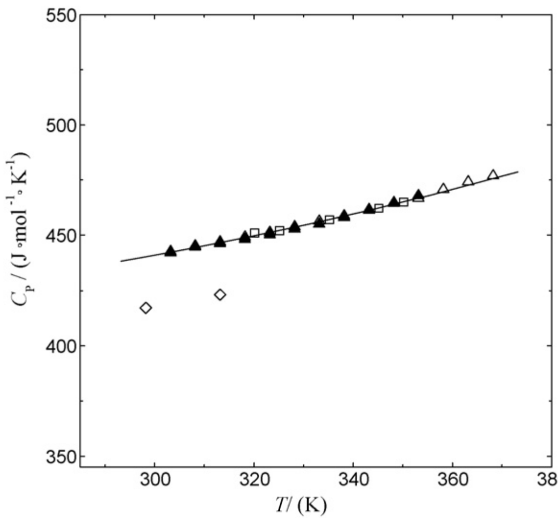

Fig. 1. Heat capacity of pure [Bmim][triflate]: ▲, this work; ◇, Fredlake et al. [1]; □, Diedrichs and Gmehling [6]; △, Yu et al. [22]; and line, calculated using Eq. (1).

Table 1
Molar heat capacities of [Bmim][MeSO$_4$] (1) + H$_2$O (2).

T (K)	Molar heat capacity, C_P and excess molar heat capacity C_P^E (J mol^{-1} K^{-1})							
	$x_1 = 0.20$		$x_1 = 0.40$		$x_1 = 0.60$		$x_1 = 0.80$	
	C_P	C_P^E	C_P	C_P^E	C_P	C_P^E	C_P	C_P^E
303.2	140	1.9	203	1.9	265	0.03	326	−1.9
308.2	142	2.8	205	2.7	267	1.3	328	−0.7
313.2	142	3.3	207	3.7	269	2.4	331	0.6
318.2	143	3.8	209	4.9	272	3.8	334	1.8
323.2	145	4.5	210	5.7	275	5.5	337	2.8
328.2	146	5.2	212	6.7	277	6.5	340	4.2
333.2	147	5.8	214	7.8	280	7.8	342	5.1
338.2	148	6.7	216	8.7	282	8.9	346	6.7
343.2	149	7.4	218	9.5	285	10.7	349	8.1
348.2	151	8.2	220	10.8	287	11.4	352	9.2
353.2	152	8.8	222	11.8	291	13.2	355	10.8

$$C_P\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = 345.39 + 0.16823\,(T/\mathrm{K}) + 4.95 \times 10^{-4}\,(T/\mathrm{K})^2 \tag{1}$$

Eq. (1) was used in the evaluation of molar heat capacity of pure [Bmim][triflate] for the calculation of excess molar heat capacity, C_P^E. The determined constants in Eq. (1) correlated well the present C_P data of pure [Bmim][triflate] from this work together with the selected literature values as shown by average absolute percentage deviation (AAD) of about 0.1%. The equation for AAD was defined in our recent work [22].

After the validation of experimental methods, the values of C_P for aqueous binary solutions of [Bmim][MeSO$_4$] and [Bmim][triflate] were measured for temperature range of 303.2–353.2 K at normal atmospheric pressure. Tables 1 and 2 present the C_P measurements and the calculated excess molar heat capacity of a mixture, C_P^E, of the studied binary solutions. As presented in Tables 1 and 2, the values of C_P for the studied binaries increase as the temperature and composition (IL concentration) increases.

In this work, the expression for C_P^E, defined by Lide and Kehiaian [23] was applied and is written as

$$C_P^E = C_P - \sum_i x_i C_{P,i} \tag{2}$$

Table 2
Molar heat capacities of [Bmim][triflate] (1) + H$_2$O (2).

T (K)	Molar heat capacity, C_P and excess molar heat capacity C_P^E (J mol^{-1} K^{-1})							
	$x_1 = 0.20$		$x_1 = 0.40$		$x_1 = 0.60$		$x_1 = 0.80$	
	C_P	C_P^E	C_P	C_P^E	C_P	C_P^E	C_P	C_P^E
303.2	149	−0.2	223	0.6	295	−0.7	366	−2.4
308.2	150	0.6	225	1.8	298	1.0	370	−1.1
313.2	151	1.4	227	3.2	301	2.5	372	−0.2
318.2	152	1.7	229	4.2	304	4.2	376	1.0
323.2	153	2.3	231	5.4	307	5.6	378	2.0
328.2	154	3.1	234	7.1	310	7.2	381	3.1
333.2	155	3.7	236	8.6	313	8.9	385	4.6
338.2	157	4.5	238	9.5	316	10.7	388	5.4
343.2	158	5.1	241	10.9	319	12.2	392	7.1
348.2	159	6.0	243	12.1	323	13.8	395	8.1
353.2	161	6.7	246	13.8	325	15.2	398	9.3

where $C_{P,i}$ is the molar heat capacity of the pure component, i. The molar heat capacity of the pure component, i.e., for H_2O, [Bmim][$MeSO_4$], and [Bmim][triflate] were determined from Osborne et al. [24], Yu et al. [22], and Eq. (1), respectively. The determined C_P^E values using Eq. (2) are also presented in Tables 1 and 2. As presented in these tables, the determined C_P^E increases gradually as the temperature increases. The calculated C_P^E of the studied binaries describe a similar behavior overall: they show a positive value with exemptions of some data points at low temperature of 303.2 K and high IL mole fraction of $x_1 = 0.8$.

The temperature and compositional dependence of the excess molar heat capacity for the studied binary mixtures was correlated using the Redlich–Kister equation given as

$$C_P^E\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{3}$$

where A_i is assumed to follow the equation

$$A_i = a_{i,0} + a_{i,1}(T/\mathrm{K}) \tag{4}$$

The parameters $a_{i,0}$ and $a_{i,1}$ for the studied binaries were determined by fitting the C_P data from this work using Eq. (3) and the results are presented in Table 3. The number of terms (A_i), in Eq. (3), which should be used to represent the excess molar heat capacity, depends on the degree of complexity of the binary systems. In this work, three terms in Eq. (3) were found to be sufficient to correlate the present measurements as shown by a reasonable overall AAD of 0.1 and 8.3% for C_P and C_P^E calculations, respectively, for a total of 88 data points. Figs. 2 and 3 plot the calculated and experimental C_P^E values for [Bmim][$MeSO_4$] + H_2O and [Bmim][triflate] + H_2O, respectively. Eq. (3) successfully represented the temperature and compositional dependence of the excess molar heat capacity for the studied binary solutions as shown in Fig. 2a and b.

The present calculations of C_P^E were also compared to the calculated values obtained from the recent work of Garcia-Miaja et al. [13] for the investigated binaries. Fig. 3 shows such comparison. As seen in this figure, the two sets of calculated values of C_P^E were not consistent with each other. Such differences could be accounted on several aspects such as the applied method for the measurement of C_P and the data used to evaluate the C_P^E values. Garcia-Miaja et al. [13] used a Calvet microcalorimeter, which has been modified in order to stir the mixture, needed for most of their studied samples due to the ILs high viscosity. But they [13] also admitted that the stirring procedure, consequently, increases the experimental uncertainty to about 4%. In our present C_P measurements, no stirring procedure was considered. The data used to fit the parameters of the Redlich–Kister equation also affect significantly the results of calculations. Our calculations supplied data from previously obtained equations for pure systems (water and ILs) while Garcia-Miaja et al. [13] used data from their own experiments to evaluate the excess heat capacity.

Table 3
Parameters of excess molar heat capacity equation for the studied binaries.

System	i	Parameters		No. of data points	AAD%	
		$a_{i,0}$	$a_{i,1}$		C_P	C_P^E
[Bmim][$MeSO_4$] + H_2O	1	−276.51	0.92590	44	0.1	11.5
	2	−202.83	0.60300			
	3	−253.18	0.79310			
[Bmim][triflate] + H_2O	1	−368.45	1.21790	44	0.1	5.0
	2	−174.47	0.53561			
	3	29.812	−0.18229			
	Overall			88	0.1	8.3

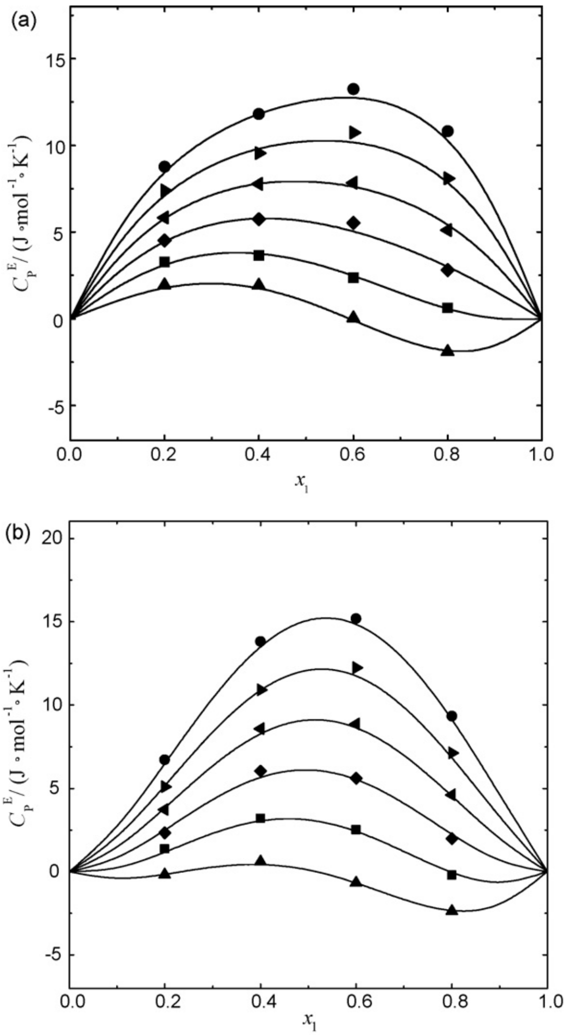

Fig. 2. (a) Excess molar heat capacity of [Bmim][$MeSO_4$] (1) + H_2O (2): ▲, 303.2 K; ■, 313.2 K; ♦, 323.2 K; ◄, 333.2 K; ►, 343.2 K; ●, 353.2 K; and lines, calculated using Eq. (3). (b) Excess molar heat capacity of [Bmim][triflate] (1) + H_2O (2): ▲, 303.2 K; ■, 313.2 K; ♦, 323.2 K; ◄, 333.2 K; ►, 343.2 K; ●, 353.2 K; and lines, calculated using Eq. (3).

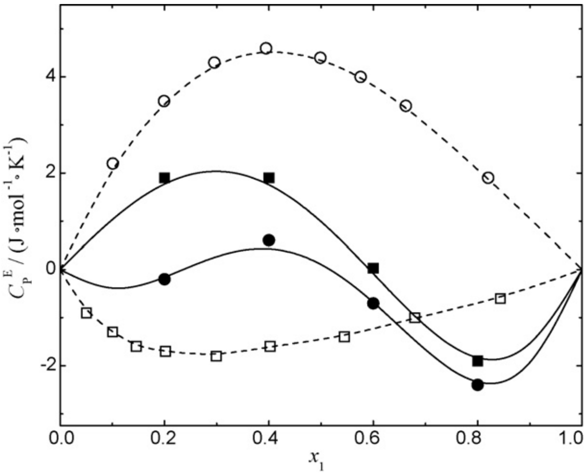

Fig. 3. Excess molar heat capacity of the studied binaries at 303.15 K: (■, this work; □, Garcia-Miaja et al. [13]), [Bmim][$MeSO_4$] + H_2O; (●, this work; ○, Garcia-Miaja et al. [13]), [Bmim][triflate] + H_2O; and lines, smoothed.

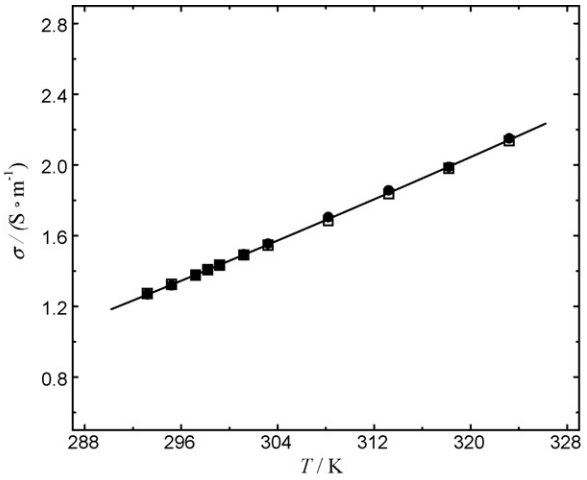

Fig. 4. Electrolytic conductivity of standard KCl solution: ●, this work; □, analyzed values by the Merck Calibration Laboratory for pH value and electrical conductivity; and line, smoothed.

3.2. Electrolytic conductivity

The present apparatus and experimental method for σ measurements were justified by measuring the σ data of standard KCl solution and comparing it to the measured value of Merck Calibration Laboratory before measuring the σ of the actual sample. This was also done to ensure that the conductivity cell is functioning properly. Fig. 4 shows a sample result of the σ data of standard KCl solution along with the analyzed values of Merck.

Upon ensuring that the conductivity cell was functioning properly, the σ data for the studied binaries were measured for temperatures ranging from 293.2 to 353.2 K at normal atmospheric pressure. Fig. 5a and b show the plots of the present σ measurements for aqueous binary systems [Bmim][MeSO$_4$] + H$_2$O and [Bmim][triflate] + H$_2$O at different temperatures and compositions. As shown in these figures, the σ values of the studied systems decrease as the concentration increase and increase as the temperature increase. This behavior is usual, as expected.

The temperature and composition dependence of the measured σ were correlated by modifying the empirical equation developed by Graber et al. [20] for ternary aqueous solutions containing poly(ethylene) glycol (PEG). The modified form of the equation is written as

$$\sigma = x_1 \exp[B_1 + B_2 T^{0.5} + B_3 x_1^{0.5}] + B_4 + B_5 T^{0.5} + B_6 x_1^{0.5} \tag{5}$$

where σ is the electrical conductivity in (S m^{-1}), x_1 the mole fraction of ionic liquid, T the absolute temperature in K, and B_i is the equation parameters. The parameters B_i were determined by fitting the σ values from this work using Eq. (5) and the results are presented in Table 4. The determined parameters B_i correlated well the present σ measurements as shown by an overall AAD of about 3.3% for a total of 104 data points. The results of calculations using Eq. (5) were also shown in Fig. 5a and b for [Bmim][MeSO$_4$] + H$_2$O and [Bmim][triflate] + H$_2$O, respectively. As shown in these figures, Eq. (5) reasonably represented the obtained σ data.

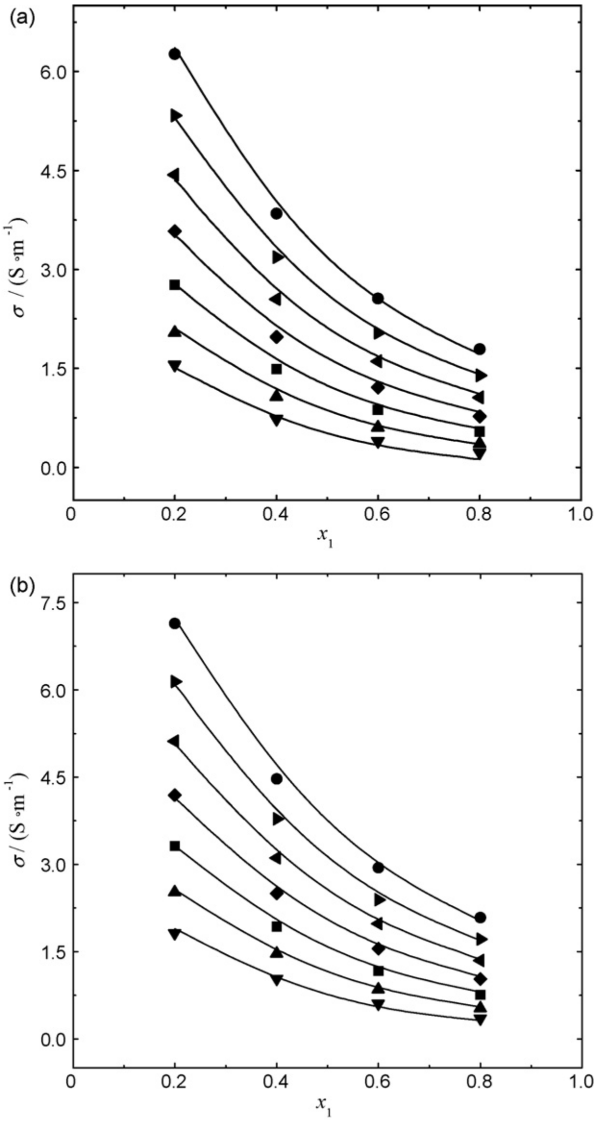

Fig. 5. (a) Electrolytic conductivity of [Bmim][MeSO$_4$] (1) + H$_2$O (2): ▼, 293.2 K; ▲, 303.2 K; ■, 313.2 K; ♦, 323.2 K; ◄, 333.2 K; ►, 343.2 K; ●, 353.2 K; and lines, calculated using Eq. (5). (b) Electrolytic conductivity of [Bmim][triflate] (1) + H$_2$O (2): ▼, 293.2 K; ▲, 303.2 K; ■, 313.2 K; ♦, 323.2 K; ◄, 333.2 K; ►, 343.2 K; ●, 353.2 K; and lines, calculated using Eq. (5).

Table 4
Parameters of Eq. (5) for the studied binaries.

System	i	Parameters B_i	No. of data points	AAD%
[Bmim][MeSO$_4$] + H$_2$O	1	−4.2757	52	4.3
	2	0.57241		
	3	−6.6634		
	4	−9.4967		
	5	0.45642		
	6	1.4381		
[Bmim][triflate] + H$_2$O	1	−2.6108	52	2.2
	2	0.48871		
	3	−6.3170		
	4	−9.2917		
	5	0.35862		
	6	2.8756		
	Overall		104	3.3

4. Conclusions

The molar heat capacities and electrolytic conductivities of [Bmim][MeSO$_4$] + H$_2$O and [Bmim][triflate] + H$_2$O were measured over the temperature range from 303.2 to 353.2 K and from 293.2 to 353.2 K, respectively, over a complete composition range. The C_P was measured using a DSC and the σ was measured using a conductivity meter. The C_P and σ values of some substances have been measured too and compared to available literature data in order to validate the accuracy of the apparatus and experimental procedures used. For C_P and σ measurements validation, pure [Bmim][triflate] and standard KCl solution were used, respectively. The C_P and σ values from this work were found to be in good agreement with the available literature data. The measured C_P and σ of the studied systems were presented as a function of temperature and composition. An excess molar heat capacity expression using the Redlich–Kister equation and a modified empirical equation proposed by other researcher were used to correlate the temperature and compositional dependence of the measured C_P and σ of the studied systems. The correlations successfully represented the measured C_P and σ data as shown by reasonable AAD values of 0.1 and 3.3% for C_P and σ calculations, respectively.

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