Thermochimica Acta 482 (2009) 42–48

Contents lists available at ScienceDirect

Thermochimica Acta

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

Heat capacities and electrical conductivities of 1-*n*-butyl-3-methylimidazolium-based ionic liquids

Ya-Hung Yu, Allan N. Soriano, Meng-Hui Li*

R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan

ARTICLE INFO

Article history:
Received 28 May 2008
Received in revised form 20 October 2008
Accepted 21 October 2008
Available online 30 October 2008

Keywords:
Heat capacity
Electrical conductivity
[Bmim]-based ionic liquids

ABSTRACT

Here we presented the heat capacities and electrical conductivities of four [Bmim (1-*n*-butyl-3-methylimidazolium)]-based ionic liquids. The heat capacities were measured using a differential scanning calorimeter in the temperature range from 303.2 to 358.2 K. The electrical conductivities were measured over temperature range from 293.2 to 353.2 K using conductivity meter. The estimated uncertainties of heat capacity C_p and electrical conductivity σ measurements were ±2% and ±1%, respectively. The measurements were presented as a function of temperature. The temperature dependency of the C_p value was correlated using an empirical equation. A modified version of Vogel–Tamman–Fulcher equation was employed to describe the temperature dependency of σ values. The correlations give satisfactory results. The presented results were in good agreement with the available literature data.

1. Introduction

Solutions of alkanolamines are industrially important compounds because they are effective on CO_2 removal. But the used of these compounds usually requires higher energy consumption and operational cost, and also comes with solvent pollutions. On the other hand, in recent years, there has been a new class of compound, termed as green solvents, which is now recognized as a versatile alternative to aqueous alkanolamine solutions. This class is known as ionic liquids (ILs). ILs are organic salts that are liquids at ambient temperature and because of their unique properties, such as low volatility, non-flammability, high thermal stability, and high solvation capacity [1–3], they have attracted a number of research groups such that these groups are now doing a systematic measurement and collection of the thermophysical and transport properties of ILs [4–16].

The heat capacity C_p and electrical conductivity σ are two of the basic pure component properties for any substance and its knowledge is essential for many engineering applications. For most ILs these values are still lacking. For the C_p data, the thorough studied ILs were those of ammonium-, pyridinium-, pyrrolidinium-, bis[(trifluoromethyl)sulfonyl]amide- and imidazolium-based ILs [2,4,6,12–15,17–26]. In the C_p measurement of imidazolium-based ILs most of the work clustered on hexyl- and butyl-3-methylimidazolium, but on a limited range of temperatures and pressures [2,12–15,17]. As for the σ data, only those of ammonium, pyrrolidinium, bis[(trifluoromethyl)sulfonyl]amide were the widely studied, not much on imidazolium-based ILs [5,9,11,26–31]. Hence, heat capacities and electrical conductivities for four [Bmim]-based ILs have been investigated on this work. The investigated ILs were [Bmim][BF_4 (tetrafluoroborate)], [Bmim][PF_6 (hexafluorophosphate)], [Bmim][$MeSO_4$ (methylsulfate)], and [Bmim][CF_3SO_3 (trifluoromethanesulfonate)]. The heat capacities were measured over the temperature range from 303.2 to 358.2 K and standard pressure, the electrical conductivities over temperature range from 293.2 to 353.2 K and standard pressure.

2. Experimental

2.1. Sample

All ILs used in this work were supplied by TCI Co. except for [Bmim][$MeSO_4$] which was from STREM Co. Table 1 shows the purity of the investigated ILs. Among the many reasons for differences in most experimental data for some thermodynamic properties of ILs the question of purity especially the water content of the investigated samples is one of the most serious. In this regard, the water content of the investigated ILs are also presented in Table 1. Fig. 1 shows the structures of the investigated ILs. The ILs were used without further purification. The liquid water used for the calibration of the calorimeter was deionized, with a resistivity of 18.3 M Ωcm and with a total organic carbon content of less than 15 ppb, produced by Barnstead Thermodyne, model Easy Pure 1052. The standard KCl solution used for the calibration

---

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

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.10.015

Table 1
Ionic liquids investigated in this work.

Ionic liquid	Abbreviation	Purity	Water content
1-Butyl-3-methylimidazolium tetrafluoroborate	$[Bmim][BF_4]$	≥0.990	≤0.002
1-Butyl-3-methylimidazolium hexafluorophosphate	$[Bmim][PF_6]$	≥0.990	≤0.002
1-Butyl-3-methylimidazolium methylsulfate	$[Bmim][MeSO_4]$	≥0.980	≤0.009
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	$[Bmim][CF_3SO_3]$	≥0.981	≤0.007

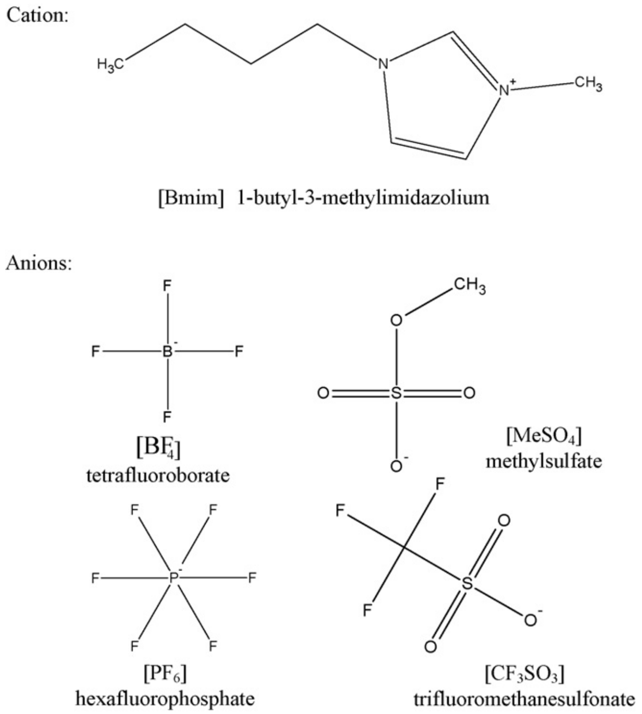

Fig. 1. Cation and anions of the investigated ionic liquids.

of the conductivity meter was supplied by Merck, with $c = 0.1$ N and electrolytic conductivity of 1.415 mS cm^{-1} at 298.15 K.

2.2. Heat capacity measurements

The heat capacity was measured using the differential scanning calorimeter (DSC) consisting of a DSC-2010 and a thermal analysis controller from TA Instruments. The DSC operating range is from the room temperature to 998.15 K. Both the temperatures and the heat flow associated with transitions in materials can be easily and rapidly measured with the system. The DSC operates with a temperature repeatability of ±0.1 K. Calorimetric sensitivity is 1 μW (rms). The calorimetric precision is ±1% based on measurements of metal samples. The purge gas is nitrogen with a flow rate of 40 mL min^{-1}. The heating rate was set to be 5 K min^{-1}. By using the sample encapsulating press, the liquid sample was prepared within a hermetic sample pan. The internal volume of the hermetic pan is approximately 10 mm^3. Sample mass is in the range of 15–20 mg. Five replicate runs were carried out for each measurement. The apparatus and the experimental procedures were the same as those described by Chiu et al. [32].

2.3. Electrical conductivity measurements

The electrical conductivity was measured using SC-170 conductivity meter manufactured by Suntex. The uncertainty of the conductivity measurement is ±1% for readings below 50 mS cm^{-1}. The temperature was monitored using digital thermometer (model 3002, CROPICO), with an uncertainty of ±0.01 K. A fixed volume of sample (3 mL) was placed in a test tube and was placed in a water bath where the temperature was controlled. The conductivity cell was first adjusted to 0 in the air followed by the calibration of standard KCl solution before it was put in the sample to be measured. The calibration of this equipment is the same as those described by Widegren et al. [5]. The conductivity cell was then washed by deionized water and ethanol to remove any adhering IL, and dried. To preserve the conductivity cell it was placed in water or in dry air before used for the next measurement. The measurements were done in five replicate runs.

3. Results and discussion

3.1. Heat capacity

The equation used to evaluate the C_p were the same as those describe by Chiu et al. [32]. To justify the accuracy of the DSC, the C_p of liquid water was measured and compared to the data of Osborne et al. [33]. They [33] were able to measure the heat capacity of water with an uncertainty of ±0.0001 to ±0.0002 J g^{-1} K^{-1} at close intervals of temperature (1 K) by using a large adiabatic calorimeter. Table 2 shows the comparison of C_p data between Osborne et al. [33] and this work. The present experimental results for water were in good agreement with the C_p values of Osborne et al. [33] as shown by an average absolute percentage deviation (AAD%) of 0.11. The AAD% was defined as

$$\mathrm{AAD\%} = \frac{1}{n}\sum_{i}^{n}\frac{|(\varepsilon_{\mathrm{lit}} - \varepsilon_{\mathrm{expt}})|_i}{\varepsilon_{\mathrm{lit}}} \tag{1}$$

where $\varepsilon_{\mathrm{lit}}$ is the literature value, $\varepsilon_{\mathrm{expt}}$ the experimental value, and n the number of data points. On the basis of comparison with literature values for water, the uncertainty of the C_p measurements is estimated to be ±2%.

After the calibration process, the C_p values of four [Bmim]-based ionic liquids were measured for temperatures ranging from

Table 2
Heat capacity C_p of liquid water.

T (K)	Heat capacity, C_p (J g^{-1} K^{-1})						
	Osborne et al. [33]	This study					
		Run 1	Run 2	Run 3	Run 4	Run 5	Mean value
303.2	4.1785	4.20	4.17	4.17	4.18	4.20	4.18 ± 0.013
308.2	4.1782	4.20	4.17	4.17	4.18	4.19	4.18 ± 0.013
313.2	4.1786	4.20	4.17	4.17	4.18	4.19	4.18 ± 0.012
318.2	4.1795	4.20	4.17	4.17	4.18	4.20	4.18 ± 0.013
323.2	4.1807	4.20	4.17	4.17	4.19	4.20	4.19 ± 0.013
328.2	4.1824	4.200	4.18	4.17	4.19	4.20	4.19 ± 0.012
333.2	4.1844	4.20	4.18	4.18	4.19	4.20	4.19 ± 0.012
338.2	4.1868	4.20	4.18	4.18	4.19	4.20	4.19 ± 0.012
343.2	4.1896	4.21	4.18	4.18	4.19	4.21	4.19 ± 0.012
348.2	4.1928	4.21	4.19	4.18	4.20	4.21	4.20 ± 0.012
353.2	4.1964	4.21	4.19	4.19	4.20	4.21	4.20 ± 0.012
AAD%							0.11

Table 3
Heat capacity C_p of the investigated ionic liquids.

T (K)	Heat capacity, C_p (J g^{-1} K^{-1})			
	[Bmim][BF$_4$]	[Bmim][PF$_6$][a]	[Bmim][MeSO$_4$]	[Bmim][CF$_3$SO$_3$]
293.2	1.523[b]	–	1.906[b]	1.606[b]
298.2	1.640[c]	–	1.831[c]	1.720[c]
303.2	1.63 ± 0.006	1.45 ± 0.013	1.50 ± 0.009	1.54 ± 0.010
308.2	1.64 ± 0.003	1.47 ± 0.018	1.52 ± 0.008	1.54 ± 0.011
313.2	1.65 ± 0.004	1.48 ± 0.017	1.53 ± 0.008	1.55 ± 0.012
318.2	1.66 ± 0.005	1.49 ± 0.016	1.53 ± 0.007	1.56 ± 0.013
323.2	1.67 ± 0.009	1.49 ± 0.017	1.54 ± 0.007	1.57 ± 0.014
328.2	1.68 ± 0.008	1.50 ± 0.016	1.55 ± 0.008	1.57 ± 0.015
333.2	1.69 ± 0.005	1.51 ± 0.016	1.56 ± 0.007	1.58 ± 0.014
338.2	1.70 ± 0.005	1.52 ± 0.016	1.57 ± 0.008	1.59 ± 0.015
343.2	1.71 ± 0.008	1.53 ± 0.016	1.57 ± 0.007	1.60 ± 0.015
348.2	1.72 ± 0.008	1.55 ± 0.017	1.59 ± 0.008	1.61 ± 0.017
353.2	1.73 ± 0.007	1.56 ± 0.015	1.59 ± 0.007	1.62 ± 0.017
358.2	1.74 ± 0.008	1.56 ± 0.009	1.60 ± 0.009	1.63 ± 0.018

[a] No estimated values from Chueh and Swanson [35] and Missenard [34] due to insufficient data.
[b] Estimated from Chueh and Swanson [35].
[c] Estimated from Missenard [34].

303.2 to 358.2 K. For systems, in which literature values of heat capacities were available, a comparison was made to assure that the measured data in this study were correct. For the purpose of comparison, C_p values for the investigated ILs were estimated from the group contribution methods of Missenard [34] and Chueh and Swanson [35] but due to the limited temperature range and group contributions of elemental and functional group parameters, the calculated C_p values from the group contribution method was not totally apply to the specified temperature range and to some ionic liquids. For instance in the evaluation of C_p for [Bmim][BF$_4$], the estimated C_p values from Missenard [34] and Chueh and Swanson [35] group contribution methods were evaluated only at temperatures 298.2 and 293.2 K, respectively, furthermore, since there is no available elemental parameter for boron (B), the work of Benson [36] was considered to evaluate the elemental contribution of B. Furthermore, since there is no available elemental parameter for phosphorous (P), the C_p for [Bmim][PF$_6$] using the group contribution methods were not able to evaluate.

The measured C_p values for the investigated ILs along with the estimated values from the group contribution methods of Missenard [34] and Chueh and Swanson [35] were presented in Table 3 and also shown from Figs. 2 to 6. Fig. 2 shows the measured C_p values of [Bmim][BF$_4$] from this work along with the available literature values. As seen from this figure, the measured C_p of [Bmim][BF$_4$] in this work were consistent with the data of Waliszewski et al. [6] and Rebelo and co-workers [37]. The C_p data of van Valkenburg et al. [8] and Fredlake et al. [14] appear to have a lower C_p values compared to Waliszewski et al. [6], Rebelo and co-workers [37], and this work. On the other hand, the C_p data of Kim et al. [13] appear to have a higher C_p values compared to Waliszewski et al. [6], Rebelo and co-workers [37] and this work. The values of C_p obtained from the group contribution method of Chueh and Swanson [35] at 293.2 K was a little consistent with the data of Waliszewski et al. [6], Rebelo and co-workers [37], and this study while the group contribution method of Missenard [34] at 298.2 K was consistent with the data point of Fredlake et al. [14]. The temperature dependence of the C_p values from this work were slightly weaker compared to that of the data of Waliszewski et al. [6] and Rebelo and co-workers [37].

Fig. 3 shows the measured C_p data of [Bmim][PF$_6$] from this work along with the available literature values. As shown in this figure, the present C_p data of [Bmim][PF$_6$] from this work were in good

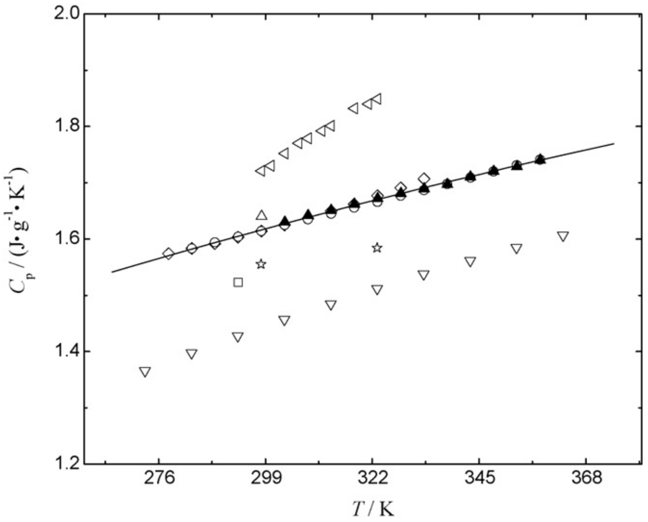

Fig. 2. Heat capacity of [Bmim][BF$_4$]: (▲) this work; (△) Missenard [34]; (□) Chueh and Swanson [35]; (◇) Rebelo et al. [25]; (◁) Kim et al. [13]; (☆) Fredlake et al. [14]; (○) Waliszewski et al. [6]; (▽) van Valkenburg et al. [8].

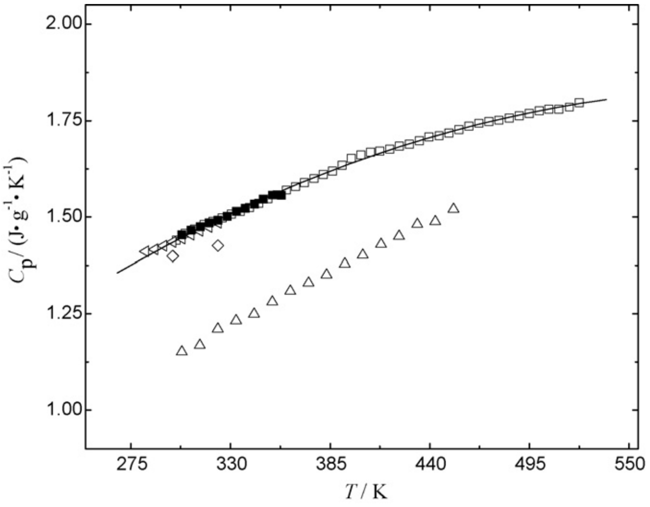

Fig. 3. Heat capacity of [Bmim][PF$_6$]: (■) this work; (△) Holbrey et al. [2]; (□) Kabo et al. [38]; (◇) Fredlake et al. [14]; (◁) Troncoso et al. [10].

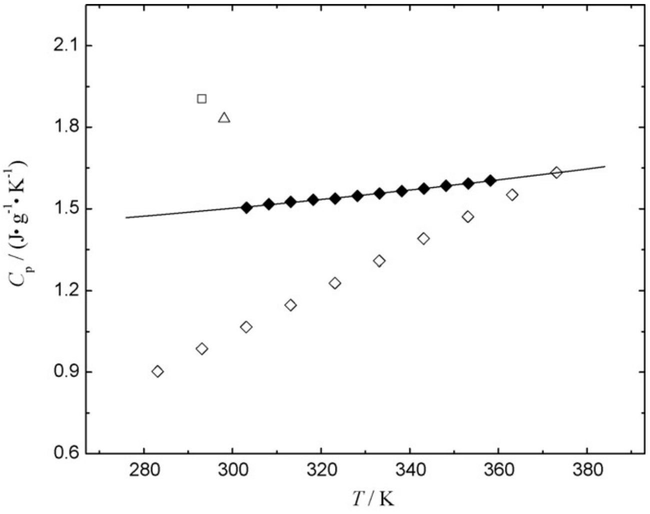

Fig. 4. Heat capacity of [Bmim][MeSO$_4$]: (♦) this work; (△) Missenard [34]; (□) Chueh and Swanson [35]; (◇) Fernandez et al. [15].

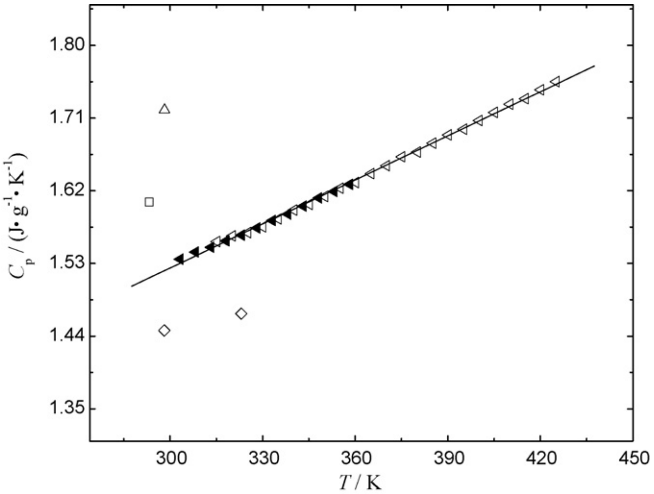

Fig. 5. Heat capacity of [Bmim][CF_3SO_3]: (◄) this work; (△) Missenard [34]; (□) Chueh and Swanson [35]; (◇) Fredlake et al. [14]; (◁) Diedrichs and Gmehling [4].

agreement with the data of Troncoso et al. [10] and Kabo et al. [38]. The C_p data of Holbrey et al. [2] and Fredlake et al. [14] seem to have a lower C_p values compared to Troncoso et al. [10], Kabo et al. [38], and this work. The group contribution methods of Chueh and Swanson [35] and Missenard [34] were not able to apply due to insufficient data, as previously discussed. The temperature dependence of the C_p values obtained from this work were slightly weaker compared to that of Troncoso et al. [10] and Kabo et al. [38].

The measured C_p data of [Bmim][$MeSO_4$] from this work together with the available literature value is shown in Fig. 4. In this figure, the C_p values of Fernandez et al. [15] were very inconsistent with the measured C_p values from this work. The obtained C_p values from the group contribution methods [34,35] were a bit closer to the measured C_p values from this work. The temperature dependence of the C_p values from this work were weaker compared to the C_p values of Fernandez et al. [15]. Fig. 5 shows the measured C_p data of [Bmim][CF_3SO_3] from this work along with the available literature values. The measured C_p data of [Bmim][CF_3SO_3] from this work were in excellent agreement with the data of Diedrichs and Gmehling [4] while the C_p data of Fredlake et al. [14] appear to have a lower C_p values. The temperature dependence of the C_p values from this work were almost similar with that of Diedrichs and Gmehling [4].

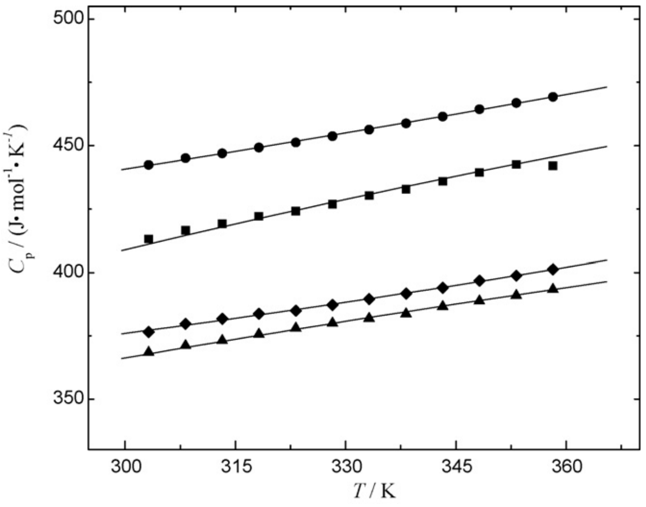

Fig. 6. Heat capacity of [Bmim]-based ionic liquids (in molar basis): ((▲) [Bmim][BF_4]; (■) [Bmim][PF_6]; (♦) [Bmim][$MeSO_4$]; (●) [Bmim][CF_3SO_3]) experimental results from this work; and solid lines, calculated using Eq. (2).

Table 4
Calculation of heat capacity of the investigated ionic liquids using Eq. (2).

System	T (K)	No. of data points	Reference	(AAD%)[a]
[Bmim][BF_4]	278.15–333.15	12	[25]	0.25
	283.15–358.15	16	[6]	0.14
	303.2–358.2	12	This study	0.10
[Bmim][PF_6]	300.05–524.87	1528	[38]	0.23
	289.1–309.15	11	[10]	0.41
	303.2–358.2	12	This study	0.27
[Bmim][$MeSO_4$]	303.2–358.2	12	This study	0.08
[Bmim][CF_3SO_3]	315.15–425.15	23	[4]	0.09
	303.2–358.2	12	This study	0.06
Overall		1638		0.22

[a] Calculated from Eq. (2).

In Fig. 6, the values of C_p for the four [Bmim]-based ILs were shown. Among the four ILs, [Bmim][BF_4] was observed to have the strongest temperature dependence of C_p while [Bmim][$MeSO_4$] has the weakest temperature dependence of C_p. At 333.2 K, the values of C_p for [Bmim]-based ILs were in the following order: 1.689 J g^{-1} K^{-1} ([Bmim][BF_4]) > 1.583 J g^{-1} K^{-1} ([Bmim][CF_3SO_3]) > 1.556 J g^{-1} K^{-1} ([Bmim][$MeSO_4$]) > 1.514 J g^{-1} K^{-1} ([Bmim][PF_6]). Fig. 6 also shows the influence of molecular size in the temperature dependence of the C_p. In this figure, it is clearly seen that as the molecular weight increases so as the values of C_p. These observed results are the expected behavior (lower size requires lower energy to break the bonds, and so lower C_p values).

For the purpose of comparison and application, the measured C_p values of four [Bmim]-based ILs were expressed as a function of temperature as follows:

$$C_p = a_1 + a_2 T + a_3 T^2 \qquad (2)$$

where C_p is in (J g^{-1} K^{-1}) and T is in K. The parameters a_i were determined by fitting all the data from this work and from available literature data that were consistent with the present measurements. For instance, in the case of [Bmim][BF_4] the data of Waliszewski et al. [6] and Rebelo and co-workers [37] were included in determining the parameters a_i and for the case of [Bmim][$MeSO_4$] only the C_p data from this work were used to determine the parameters a_i. Table 4 presents the calculation of C_p using Eq. (2) from the selected C_p data. As presented in Table 4, the agreement of C_p measurements among different investigators is very satisfactory. The determined empirical parameters a_i for the investigated ILs are presented in Table 5. The determined empirical parameters a_i for each IL represented well the present experimental data and the selected literature data as shown by the overall AAD% of about 0.22 for a total of 1638 data points. The present empirical equation for C_p is the generalization of the C_p measurements by different investigators. This empirical equation can be applied over a wide range of temperature as it correlated well the new experimental results and the selected available literature data.

Table 5
Parameters a_i of Eq. (2) for the investigated ionic liquids.

System	a_1[a] (J g^{-1} K^{-1})	a_2[a] (×10^3 J g^{-1} K^{-2})	a_3[a] (×10^6 J g^{-1} K^{-3})
[Bmim][BF_4]	0.68274	4.0220	−2.9883
[Bmim][PF_6]	0.36792	4.7037	3.7784
[Bmim][$MeSO_4$]	1.34187	−4.6701	3.3367
[Bmim][CF_3SO_3]	1.20130	0.5791	1.7072

[a] $C_p = a_1 + a_2 T + a_3 T^2$.

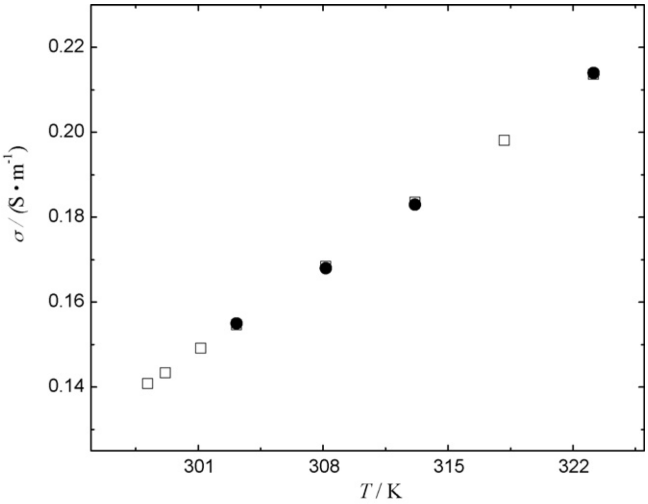

Fig. 7. A sample measurement of electrical conductivity σ for the standard KCl solution: (●) this work; and (□) analyzed values by the Merck Calibration Laboratory for pH value and electrical conductivity.

3.2. Electrical conductivity

To justify the accuracy of the conductivity meter, the σ values of the standard solution of KCl were measured. Fig. 7 shows a sample of the measured σ values of KCl solution along with the σ values of the standard solution. The measured σ values of the standard solution were made sure very consistent with the σ values of the standard solution (which was analyzed by the Merck Calibration Laboratory for pH value and electrical conductivity). These measurements were done before beginning each sample's measurements to ensure that the conductivity cell was functioning properly.

The σ values of the investigated ionic liquids were measured for temperatures ranging from 293.2 to 353.2 K. For systems, in which literature values of electrical conductivities were available, a comparison was also made to show that the measured data in this work were correct. The present measurements of σ values were presented in Table 6 and also shown from Figs. 8 to 11.

Fig. 8 shows the measured σ values of [Bmim][BF$_4$] together with the available literature data. The present measurements of σ for [Bmim][BF$_4$] were in excellent agreement with the σ data of Nishida et al. [31] and Tokuda et al. [9], as shown in Fig. 8. The measured σ values of [Bmim][PF$_6$] along with the literature data is shown in Fig. 9. In this figure, the obtained σ data from this work were in good agreement with the data of Widegren et al. [5] and Tokuda et al. [9]. The σ data of Kanakubo et al. [28] seem be a little lower than the σ data of Widegren et al. [5], Tokuda et al. [9], and

Table 6
Electrical conductivity σ of the studied ionic liquids.

T (K)	Electrical conductivity, σ (S m^{-1})			
	[Bmim][BF$_4$]	[Bmim][PF$_6$]	[Bmim][MeSO$_4$]	[Bmim][CF$_3$SO$_3$]
303.2	0.295 ± 0.008	0.114 ± 0.0012	0.217 ± 0.010	0.230 ± 0.009
308.2	0.364 ± 0.009	0.149 ± 0.0012	0.276 ± 0.009	0.286 ± 0.010
313.2	0.446 ± 0.004	0.193 ± 0.003	0.348 ± 0.011	0.358 ± 0.040
318.2	0.542 ± 0.005	0.245 ± 0.009	0.430 ± 0.007	0.437 ± 0.010
323.2	0.651 ± 0.006	0.308 ± 0.0013	0.522 ± 0.008	0.521 ± 0.010
328.2	0.783 ± 0.002	0.383 ± 0.0013	0.626 ± 0.011	0.619 ± 0.009
333.2	0.926 ± 0.003	0.468 ± 0.009	0.741 ± 0.008	0.724 ± 0.009
338.2	1.081 ± 0.001	0.556 ± 0.011	0.867 ± 0.010	0.841 ± 0.010
343.2	1.251 ± 0.002	0.664 ± 0.009	1.008 ± 0.011	0.967 ± 0.010
348.2	1.669 ± 0.007	0.917 ± 0.013	1.318 ± 0.007	1.255 ± 0.010
353.2	2.180 ± 0.001	1.214 ± 0.009	1.667 ± 0.008	1.575 ± 0.010

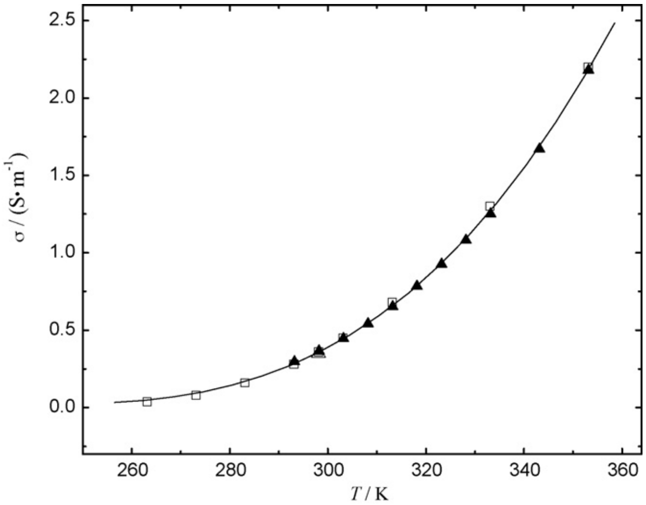

Fig. 8. Electrical conductivity of [Bmim][BF$_4$]: (▲) this work; (△) Nishida et al. [31]; (□) Tokuda et al. [9].

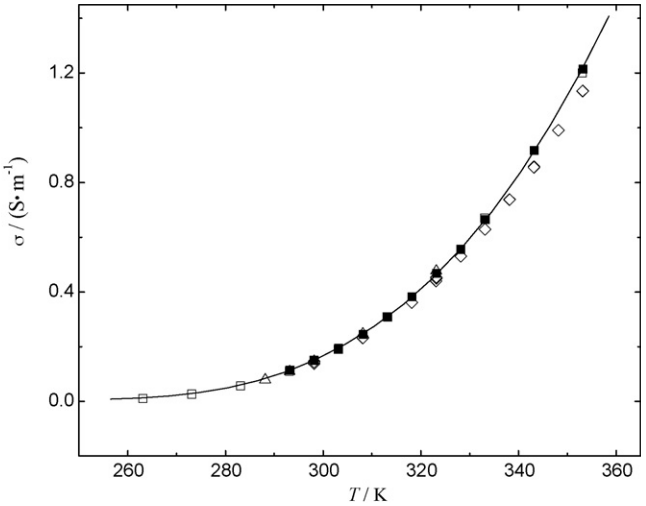

Fig. 9. Electrical conductivity of [Bmim][PF$_6$]: (■) this work; (△) Widegren et al. [5]; (□) Tokuda et al. [9]; (◇) Kanakubo et al. [28].

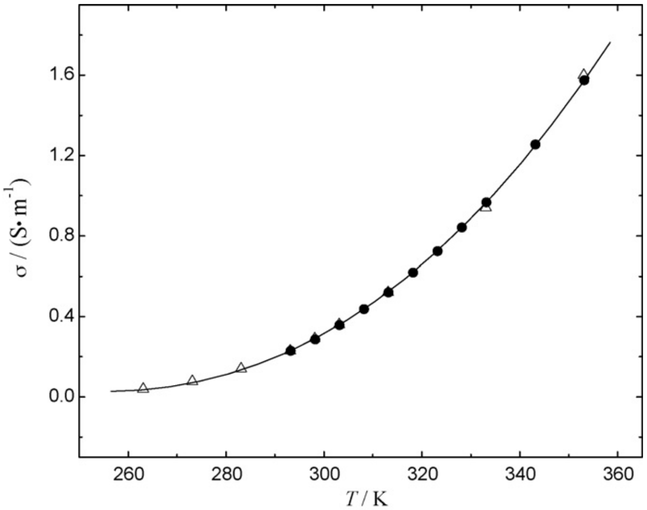

Fig. 10. Electrical conductivity of [Bmim][CF$_3$SO$_3$]: (●) this work; (△) Tokuda et al. [9].

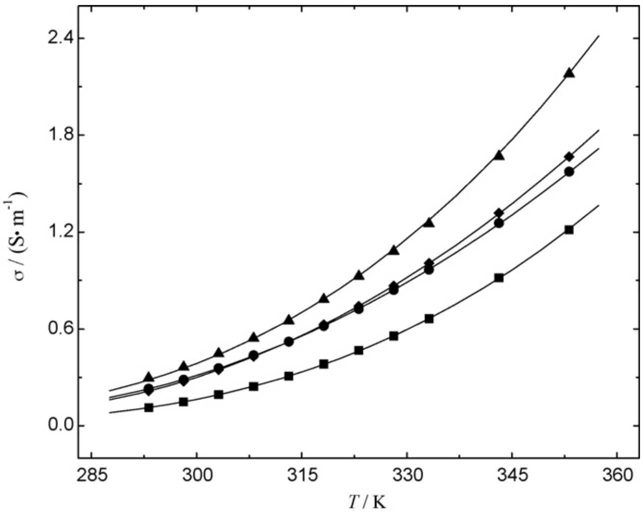

Fig. 11. Electrical conductivity of [Bmim]-based ionic liquids: ((▲) [Bmim][BF_4]; (■) [Bmim][PF_6]; (♦) [Bmim][$MeSO_4$]; (●) [Bmim][CF_3SO_3]) experimental results from this work; and solid lines, calculated using Eq. (3).

Table 7
Calculation of electrical conductivity of the investigated ionic liquids using Eq. (3).

System	T (K)	No. of data points	Reference	(AAD%)[a]
[Bmim][BF_4]	298.1	1	[31]	1.62
	263.1–373.1	10	[9]	6.84
	293.2–353.2	11	This study	1.17
[Bmim][PF_6]	288.15–323.15	5	[5]	3.16
	263.1–373.1	10	[9]	4.86
	293.2–353.2	11	This study	0.43
[Bmim][$MeSO_4$]	293.2–353.2	11	This study	0.17
[Bmim][CF_3SO_3]	263.1–373.1	10	[9]	2.94
	293.2–353.2	11	This study	0.31
Overall		97		1.92

[a] Calculated from Eq. (3).

Table 8
Parameters σ_∞, E_a, and T_g of Eq. (3) for the investigated ionic liquids.

System	σ_∞ (S m^{-1})[a]	E_a (meV)[a]	T_g (K)[a]
[Bmim][BF_4]	379.90	94.13	141.46
[Bmim][PF_6]	228.11	86.62	161.04
[Bmim][$MeSO_4$]	82.35	58.58	178.85
[Bmim][CF_3SO_3]	79.45	61.68	170.75

[a] $\sigma = \sigma_\infty \exp[-E_a/k_B(T - T_g)]$.

this work. Fig. 10 shows the measured σ values of [Bmim] [CF_3SO_3] together with the available literature data of Tokuda et al. [9]. As shown in this figure, the present measurements of σ were also in excellent agreement with the available literature data of Tokuda et al. [9]. There was no comparison made for [Bmim][$MeSO_4$] since there is still no available literature data.

The present measurements of σ for the four [Bmim]-based ILs are shown in Fig. 11. As seen in this figure, among the investigated ILs, [Bmim][BF_4] has the largest value of σ while [Bmim][PF_6] has the smallest σ value. The measured σ data for all the studied ILs has strong temperature dependence of σ. The trend of this temperature dependence was exponential. An over lapping of measured σ was observed for [Bmim][$MeSO_4$] and [Bmim][CF_3SO_3] at temperature range of 293.2–333.2 K. At 343.2 K, the values of σ for [Bmim]-based ILs were in the following order: 1.669 S m^{-1} ([Bmim][BF_4]) > 1.318 S m^{-1} ([Bmim][$MeSO_4$]) > 1.255 S m^{-1} ([Bmim][CF_3SO_3]) > 0.917 S m^{-1} ([Bmim][PF_6]). From the obtained experimental results, the influence of the anion sizes in the temperature dependence of the electrical conductivity was also interpreted. Generally, lower size molecules usually mean higher ionic mobility and so higher electrical conductivity. This was generally the major observation in the studied ILs as shown in Fig. 11, with some inconsistent behavior in the case of [Bmim][PF_6] and [Bmim][CF_3SO_3] with molecular weights of 284.18 and 288.29, respectively. This same behavior, the increase of σ value with the anion size had been observed and explained previously by Vila et al. [39] when studying the electrical conductivity of highly concentrated aqueous solution of aluminum halide salts and imidazolium-based ionic liquids. They [39] argued that while the surface electrical charge density decreases with increasing the anion size, the mobility of the anion inside a liquid plenty of free ions is augmented. Furthermore, in that work, Vila et al. [39] concluded that the anion size has two effects in electrical conductivity, i.e., the decrease of the surface electrical charge density and the effect of size for dynamical movement (hopping to adjacent holes).

For the purpose of comparison and application, the σ values of [Bmim]-based ILs were estimated using the method employed by Vila et al. [7], in which a modified version of VTF-type (Vogel–Tamman–Fulcher) equation was used and is represented as

$$\sigma = \sigma_\infty \exp\left[-\frac{E_a}{k_B(T - T_g)}\right] \qquad (3)$$

where σ_∞ is the maximum electrical conductivity (that it would have at infinite temperature), E_a the activation energy for electrical conduction (which indicates the energy needed for an ion to hop to a free hole), k_B the Boltzmann's constant, and T_g the glass transition temperature.

Using Eq. (3), the parameters σ_∞, E_a, and T_g were determined by fitting the present σ data and selected literature data, in which same criteria were used in the selection as discussed previously. Table 7 presents the calculation of σ using Eq. (3) from the different investigators. As presented in Table 7, the agreement of σ measurements among different investigators is satisfactory. The determined parameters σ_∞, E_a, and T_g for the investigated ionic liquids are presented in Table 8. The determined parameters σ_∞, E_a, and T_g for each ionic liquid correlated well the present results and the available literature data as shown by the overall AAD% of about 1.92 for a total of 97 data points. It was also observed in Table 8 that the maximum conductivity value, σ_∞, the maximum E_a and the minimum T_g correspond to [Bmim][BF_4]. Overall, the present equation for σ was the conclusion of σ measurements done by different investigators and can be applied over the studied temperature range.

4. Conclusions

The heat capacities and electrical conductivities of four [Bmim]-based ILs were measured for temperature up to 353.15 K using a DSC and a commercial conductivity meter, respectively. The C_p and σ values from this work are in good agreement with available experimental data. The measured C_p and σ of each IL was expressed and correlated as a function of temperature. The temperature dependency of the present measurements for C_p and σ were successfully correlated using an empirical and a modified VTF-type equation, respectively. The developed correlations for C_p and σ were the generalizations of the C_p and σ measurements done by different investigators and it could be applied over a wide range of temperature. The results of this work can be applied to numerous chemical processes, since C_p and σ data are essential information for its rational design.

Acknowledgment

This research was supported by a grant, NSC 97-2221-E-033-015, of the National Science Council of the Republic of China.

References

[1] R.K. Rogers, K.R. Seddon, Ionic Liquids: Industrial Applications to Green Chemistry, Oxford University Press, Washington, DC, 2002.
[2] J.D. Holbrey, W.M. Reichert, R.G. Reddy, R.D. Rogers, Ionic Liquids as Green Solvents: Progress and Prospects, Oxford University Press, Washington, DC, 2003.
[3] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 926.
[4] A. Diedrichs, J. Gmehling, Fluid Phase Equilib. 244 (2006) 68–77.
[5] J.A. Widegren, E.M. Saurer, K.N. Marsh, J.W. Magee, J. Chem. Thermodyn. 37 (2005) 569–575.
[6] D. Waliszewski, I. Stepniak, H. Piekarski, A. Lewandowski, Thermochim. Acta 433 (2005) 149–152.
[7] J. Vila, P. Gines, J.M. Pico, C. Franjo, E. Jimenez, L.M. Varela, O. Cabeza, Fluid Phase Equilib. 242 (2006) 141–146.
[8] M.E. van Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochim. Acta 425 (2005) 181–188.
[9] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, J. Phys. Chem. B 110 (2006) 19593–19600.
[10] J. Troncoso, C.A. Cerdeirina, Y.A. Sanmamed, L. Romani, L.P.N. Rebelo, J. Chem. Eng. Data 51 (2006) 1856–1859.
[11] J. Sun, M. Forsyth, D.R. MacFarlane, J. Phys. Chem. B 102 (1998) 8858–8864.
[12] Y.U. Paulechka, G.J. Kabo, A.V. Blokhin, A.S. Shaplov, E.I. Lozinskaya, Y.S. Vygodskii, J. Chem. Thermodyn. 39 (2007).
[13] K.-S. Kim, B.-K. Shin, F. Ziegler, Fluid Phase Equilib. 218 (2004) 215–220.
[14] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki, J.F. Brennecke, J. Chem. Eng. Data 49 (2004).
[15] A. Fernandez, J.S. Torrecilla, F. Rodriquez, J. Chem. Eng. Data 52 (2007) 1979–1983.
[16] W.C. Su, C.H. Chou, D.S.H. Wong, M.-H. Li, Fluid Phase Equilib. 252 (2007) 74–78.
[17] J.M. Crosthwaite, M.J. Muldoon, J.K. Dixon, J.L. Anderson, J.F. Brennecke, J. Chem. Thermodyn. 37 (2005) 559–568.
[18] A.V. Blokhin, Y.U. Paulechka, G.J. Kabo, J. Chem. Eng. Data 51 (2006) 1377–1388.
[19] Z.-H. Zhang, Z.-C. Tan, L.-X. Sun, Y. Jia-Zhen, X.-C. Lv, Q. Shi, Thermochim. Acta 447 (2006) 141–146.
[20] Y.U. Paulechka, A.V. Blokhin, G.J. Kabo, A.A. Strechan, J. Chem. Thermodyn. 39 (2007) 866–877.
[21] Z.-H. Zhang, L.-X. Sun, Z.-C. Tan, F. Xu, X.-C. Lv, J.-L. Zeng, Y. Sawada, J. Therm. Anal. 89 (2007) 289–294.
[22] G. Garcia-Miaja, J. Troncoso, L. Romani, J. Chem. Eng. Data 52 (2007) 2261–2265.
[23] A.A. Strechan, Y.U. Paulechka, A.G. Kabo, A.V. Blokhin, G.J. Kabo, J. Chem. Eng. Data 52 (2007) 1791–1799.
[24] M.J. Davila, S. Aparicio, R. Alcalde, B. Garcia, J.M. Leal, Green Chem. 9 (2007) 221–232.
[25] L.P.N. Rebelo, V. Najdanovic-Visac, Z.P. Visak, M. Nunes da Ponte, J. Szydlowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperanca, H.J.R. Guedes, H.C. de Sousa, Green Chem. 6 (2004) 369–381.
[26] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, J. Phys. Chem. B 109 (2005) 6103–6110.
[27] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, J. Phys. Chem. B 103 (1999) 4164–4170.
[28] M. Kanakubo, K.R. Harris, N. Tsuchihashi, K. Ibuki, M. Ueno, J. Phys. Chem. B 111 (2007) 2062–2069.
[29] W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, J. Solution Chem. 35 (2006) 1337–1346.
[30] J. Vila, P. Gines, E. Rilo, O. Cabeza, L.M. Varela, Fluid Phase Equilib. 247 (2006) 32–39.
[31] T. Nishida, Y. Tashiro, M. Yamamoto, J. Fluorine Chem. 120 (2003) 135–141.
[32] L.F. Chiu, H.F. Liu, M.-H. Li, J. Chem. Eng. Data 44 (1999) 631–636.
[33] N.S. Osborne, H.F. Sitmson, D.C. Ginnings, J. Res. Natl. Bur. Stand 23 (1939) 197–260.
[34] F.A. Missenard, C.R. Acad. Sci. 260 (1965) 5521–5523.
[35] C.F. Chueh, A.C. Swanson, Chem. Eng. Prog. 69 (1973) 83–85.
[36] S.W. Benson, Thermochemical Kinetics, Wiley, New York, 1968.
[37] M.J. Earle, J.M.S.S. Esperanca, M.A. Gilea, J.N.C. Lopes, L.P.N. Rebelo, J.W. Magee, K.R. Seddon, J.A. Widegren, Nature 439 (2006) 831–834.
[38] G.J. Kabo, A.V. Blokhin, Y.U. Paulechka, A.G. Kabo, M.P. Shymanovich, J.W. Magee, J. Chem. Eng. Data 49 (2004) 453–461.
[39] J. Vila, L.M. Varela, O. Cabeza, Electr. Acta 52 (2007) 7413–7417.