Thermodynamic Properties of Imidazolium-Based Ionic Liquids: Densities, Heat Capacities, and Enthalpies of Fusion of [bmim][PF$_6$] and [bmim][NTf$_2$]

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Experimental densities, isobaric heat capacities, and enthalpies of fusion for one sample of 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF$_6$], and two samples of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][NTf$_2$], are reported. Data were obtained at atmospheric pressure and, in the case of the density and the heat capacity, within the temperature intervals (283.15 to 323.15) K and (278.15 to 333.15) K for [bmim][PF$_6$] and [bmim][NTf$_2$], respectively. A critical analysis of the effect of impurities on the measured thermodynamic properties is performed.

Introduction

Room temperature ionic liquids (RTILs) have been proposed as alternative environmentally friendly substitutes to the traditional organic solvents used in the chemical industry.[1−6] Among other advantages, their extremely low vapor pressures[7−9] can decrease the costs and pollution caused by the use of volatile solvents, and the very large number of possible combinations of cations and anions allows one to fine-tune the physical properties for specific applications. In this context, the study of the thermodynamic properties of RTILs can provide very useful information that could help to the design of efficient and nonpolluting chemical processes.

The synthesis of high-purity RTIL samples, although continuously improving, is still a difficult task. This is an important shortcoming as chemical impurities are known to affect their thermodynamic properties in a nonusual, dramatic manner.[10−12] In fact, the existing literature data show a strong scattering, much larger than that observed for traditional organic solvents. Further analysis on the effect of impurities is, therefore, highly desirable. For this purpose, (i) additional data for the historically most studied RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF$_6$], and (ii) data on two samples, obtained from different sources, of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][NTf$_2$], were determined. The properties under investigation were the density, the isobaric heat capacity, and the enthalpy of fusion. The obtained data were compared to those found in the literature. Also, comparison between the data for the two [bmim][NTf$_2$] samples was carried out.

Experimental Section

Materials. [bmim][PF$_6$] and one of the [bmim][NTf$_2$] samples were synthesized and purified in the QUILL laboratories (Belfast) according to procedues found elsewhere.[13,14] Purities were greater than 99.8 % as judged by ^{1}H NMR. The other [bmim][NTf$_2$] sample was purchased from Covalent Associates, with a certified purity greater than 99.5 %. The Cl$^-$ contents of the studied samples were 20 ppm for [bmim][PF$_6$], 130 ppm for the QUILL [bmim][NTf$_2$] sample, and 20 ppm for the Covalent Associates [bmim][NTf$_2$] sample. To reduce the water content and any traces of volatile compounds, vacuum at moderate temperature (333.15 K) was applied for 3 days before measurements.

Apparatus and Procedure. Densities ρ were measured using a DMA-5000 vibrating-tube densimeter from Anton-Paar. Calibration was performed using Milli-Q water and dry air as density standards. It is important to note that viscosity corrections needed for the RTILs, since they are high viscous liquids, are automatically made by the apparatus. The estimated uncertainty for commonly used, high-purity organic solvents is $\pm$ 0.00001 g·cm^{-3}; however, a higher uncertainty is expected for the studied liquids due to the above-mentioned high sensitivity of the physical properties to impurities. A critical review of the capabilities of this apparatus can be found elsewhere.[15]

Isobaric molar heat capacities C_p were obtained using a Micro DSCII differential scanning calorimeter from Setaram. This apparatus as well as the experimental technique have previously been described.[16] The scanning method at a rate of 0.25 K·min^{-1} was used. Calibration was performed using toluene and 1-butanol as heat capacity standards, their C_p values being taken from the literature.[17] The uncertainty in C_p for commonly used, high-purity organic solvents is estimated to be $\pm$ 0.2 J·mol^{-1}·K^{-1}.

The Micro DSCII calorimeter was also used to determine the enthalpies of fusion $\Delta_{fus}H$. In these experiments, the liquid heat capacity cells, used in C_p measurements, were replaced by batch cells. The value of $\Delta_{fus}H$ is obtained from the analysis of the heat flow versus temperature curve produced during the solid−liquid transition. For this purpose, the measuring cell was filled with an amount of RTIL, whose mass was determined using a Mettler AE-240 balance with an uncertainty of $\pm$ 1·10^{-5} g. Then, the sample was solidified by submersing it in liquid nitrogen. This has been done because of the metastability of RTILs.[18] The sample was stored in a dry cold chamber for 24 h with a view to ensure that spontaneous evolution of heat due to crystallization had ceased. Once placed into the calorimeter, the sample was heated at a scanning rate of 0.075 K·min^{-1}.

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10.1021/je060222y CCC: $30.25

Table 1. Experimental Densities ρ at Temperature T for the Studied RTILs

	ρ/g·cm^{-3}		
T/K	[bmim][PF$_6$]	[bmim][NTf$_2$]^a	[bmim][NTf$_2$]^b
278.15		1.45333	1.45498
283.15	1.37914	1.44852	1.45016
288.15	1.37483	1.44369	1.44533
293.15	1.37043	1.43889	1.44051
298.15	1.36612	1.43410	1.43573
303.15	1.36176	1.42931	1.43094
308.15	1.35752	1.42454	1.42617
313.15	1.35335	1.41978	1.42140
318.15	1.34916	1.41504	1.41666
323.15	1.34502	1.41031	1.41194
328.15		1.40560	1.40723
333.15		1.40092	1.40255

[a] QUILL Centre sample. [b] Covalent Associates sample.

Table 2. Densities: Fitting Coefficients A_i of Equation 1 and Standard Deviation s

	[bmim][PF$_6$]	[bmim][NTf$_2$]^a	[bmim] [NTf$_2$]^b
A_0	0.499047	0.55974	0.56072
A_1	−0.0006273	−0.0006682	−0.0006676
s/10^{-6}	6	12	8

[a] QUILL Centre sample. [b] Covalent Associates sample.

The enthalpy of fusion was obtained by numerical integration of the peak thus obtained. Signal calibration was performed by means of a Joule effect cell, and it was checked against $\Delta_{\text{fus}}H$ literature values of cyclohexane.[19] Using this procedure, the uncertainty in $\Delta_{\text{fus}}H$ was estimated to be about 1 %. The temperature of fusion T_{fus} was determined as the onset of the transition[20] with an uncertainty not worse than ± 0.1 K.

Results and Discussion

Density. Data have been obtained at atmospheric pressure and within (283.15 to 323.15) K for [bmim][PF$_6$] and within (278.75 to 333.15) K for the two [bmim][NTf$_2$] samples in steps of 1 K. For simplicity, we only show here (in Table 1) values at some temperatures, the whole amount of data being available as Supporting Information. Data were treated according to

$$\ln \rho = A_0 + A_1 T \tag{1}$$

where A_i are fitting coefficients whose values can be found in Table 2.

Figure 1 shows percentage deviations between our ρ data and those from literature; in the case of [bmim][NTf$_2$], deviations are plotted with respect to the QUILL sample values (obtained from eq 1). For both liquids, very large deviations are observed (note that typical deviations for commonly used organic solvents range around 0.02 %). As for [bmim][PF$_6$], it is worth noting the excellent agreement with the data of Kabo et al.[18] and of Jacquemin et al.[12] (within 0.02 %). As for [bmim][NTf$_2$], a systematic deviation of 0.1 % between the data of the two studied samples in this work is observed, which can be considered a good result as compared to typical deviations for RTILs but it is poor as compared to typical deviations for commonly used organic solvents. As both data sets were obtained using the same experimental methodology (i.e., the same apparatus with the same calibration), it is reasonable to ascribe the observed differences to different degrees of purity. In that sense, it is now believed that the main impurity sources in RTILs are the water content and the Cl$^-$ content. Taking into account that the effect of water on ρ is milder than that of Cl$^-$ [11,29] and assuming that most water is eliminated by means of the purification procedure previously described (see Experimental Section), it is reasonable to explain the differences to different Cl$^-$ contents. More specifically, the sample with higher Cl$^-$ content (i.e., the QUILL sample) has lower density (see Table 1). This result is in agreement with the well-established fact that Cl$^-$ lowers density.[11]

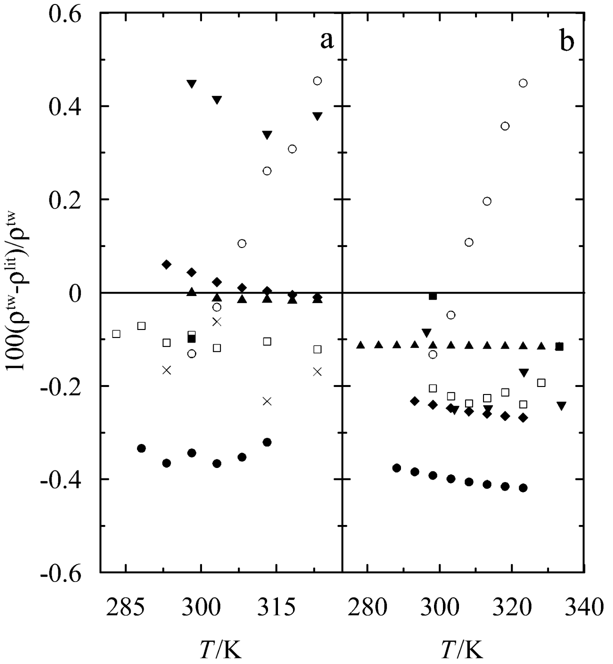

Figure 1. Percentage deviations $100\cdot(\rho^{\text{tw}} - \rho^{\text{lit}})/\rho^{\text{tw}}$ from the density data of this work (tw) with respect to literature (lit) values. (a) [bmim][PF$_6$]: ●, ref 21; ○, ref 22; ▲, ref 18; ▼, ref 23; ■, ref 24; □, ref 25; ×, ref 26; ◆, ref 12. (b) [bmim][NTf$_2$] QUILL sample: ●, ref 21; ○, ref 22; ▲, Covalent Associates sample; ▼, ref 27; ■, ref 24; □, ref 28; ◆, ref 12.

Table 3. Experimental Heat Capacities C_p at Temperature T for the Studied RTILs

	C_p/J·K^{-1}·mol^{-1}		
T/K	[bmim][PF$_6$]	[bmim][NTf$_2$]^a	[bmim][NTf$_2$]^b
283.15	400.90	559.63	558.99
288.15	402.32	562.05	561.29
293.15	404.97	564.58	564.02
298.15	407.66	567.33	566.47
303.15	410.33	569.74	569.01
308.15	413.14	572.82	572.11
313.15	415.98	575.56	575.03
318.15	418.91	578.49	577.84
323.15	421.88	581.68	581.06
328.15		584.82	584.36

[a] QUILL Centre sample. [b] Covalent Associates sample.

The isobaric thermal expansivity α_p can be directly obtained from eq 1 (note that $\alpha_p = -(\partial \ln \rho/\partial T)_p$). The fact that ln ρ versus T data are described by eq 1 clearly indicates that α_p is almost temperature-independent for the studied liquids. This behavior has been discussed previously,[29,30] and it seems to be a common feature of RTILs.

Heat Capacity. Data have been obtained at atmospheric pressure and within (283.15 to 323.15) K for [bmim][PF$_6$] and within (278.75 to 328.15) K for the [bmim][NTf$_2$] samples in steps of 0.1 K. For simplicity, we only show here (in Table 3) values at some temperatures, the whole amount of data being available as Supporting Information. Data were fitted to the expression

$$C_p = B_0 + B_1 T + B_2 T^2 \tag{2}$$

Table 4. Heat Capacities: Fitting Coefficients B_i of Equation 2 and Standard Deviation s

	[bmim][PF$_6$]^a	[bmim][NTf$_2$]^b	[bmim][NTf$_2$]^c
B_0/J·K^{-1}·mol^{-1}	388.01	569.47	590.56
B_1/10^{-1}J·K^{-2}·mol^{-1}	−4.0162	−5.4697	−6.9083
B_2/10^{-3}J·K^{-3}·mol^{-1}	1.5676	1.8088	2.0469
s/J·K^{-1}·mol^{-1}	0.09	0.10	0.11

[a] The fitting starting temperature is 285.15 K. [b] QUILL center sample. [c] Covalent Associates sample.

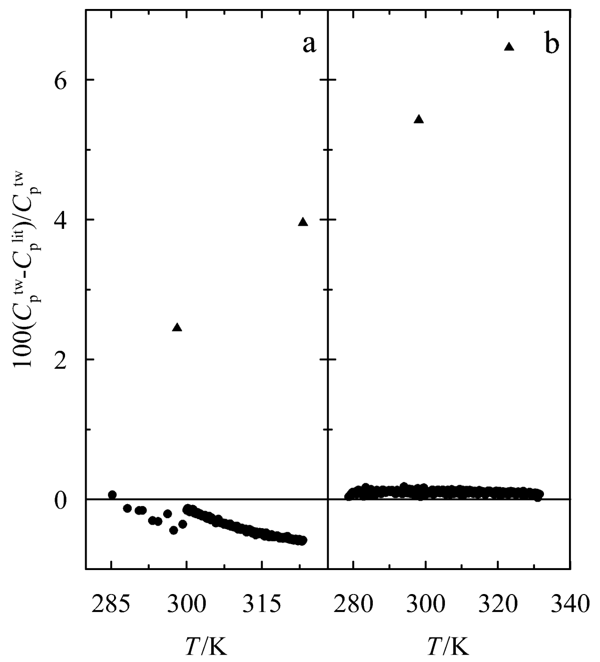

Figure 2. Percentage deviations $100\cdot(C_p^{tw} - C_p^{lit})/C_p^{tw}$ from the heat capacity data of this work (tw) with respect to literature (lit) values. (a) [bmim][PF$_6$]: ●, ref 18; ▲, ref 27. (b) [bmim][NTf$_2$] QUILL sample: ●, Covalent Associates sample; ▲, ref 27.

where B_i are fitting coefficients, whose values are listed in Table 4.

Figure 2 shows percentage deviations between our data and those from literature; again, in the case of [bmim][NTf$_2$], deviations with respect to the QUILL values (obtained from eq 2) are plotted. It must be noted that, for this property, the literature data are scarce; specifically, two sources are available for [bmim][PF$_6$] and one for [bmim][NTf$_2$]. As for [bmim][PF$_6$], good agreement is found with the data of Kabo et al.[18] It must be emphasized that this study contains data for both ρ and C_p that are in very good agreement with ours. This fact may be a direct consequence of similar purity levels for the studied samples. As for [bmim][NTf$_2$], excellent agreement is observed between the two studied samples. This situation contrasts with that observed for the density, where large differences were encountered. It is reasonable to think that Cl$^-$ content, which was regarded as the main source of discrepancies in the case of density, has little influence on C_p. A previous estimation of the effect of Cl$^-$ on the C_p of [bmim][BF$_4$] supports this statement.[29] Finally, it must be noted that the deviations from the data of Fredlake et al.[27] are significantly large and systematic for both liquids.

A further conclusion from the study of ρ and C_p has to do with the storage heat capacity $C_p\cdot V^{-1}$. From the data of Tables 1 and 3, it is deduced that both liquids have similar $C_p\cdot V^{-1}$ (around 1.95·10^6 J·m^{-3}·K^{-1} at 298.15 K).

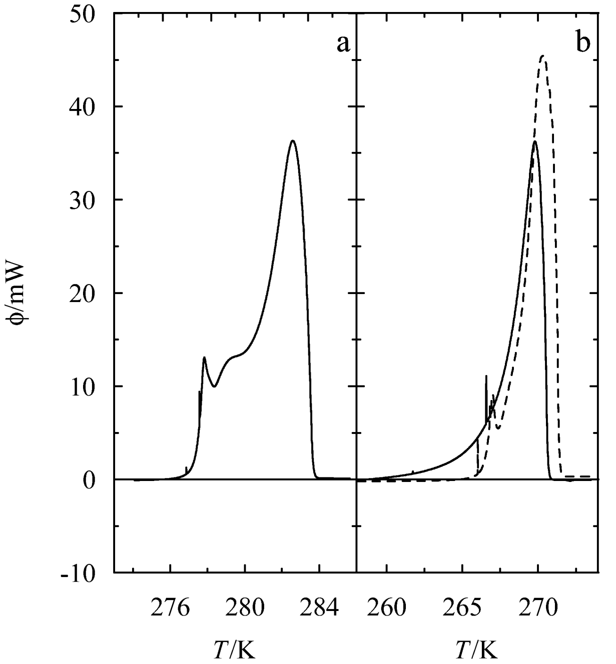

Figure 3. Heat flow ϕ against temperature T for the studied samples. (a) [bmim][PF$_6$]; (b) [bmim][NTf$_2$]: QUILL sample (solid line) and Covalent Associates sample (dashed line).

Table 5. Enthalpies $\Delta_{fus}H$ and Temperatures T_{fus} of Fusion of the Studied RTILs

	$\Delta_{fus}H$/kJ·mol^{-1}		T_{fus}/K	
	this work	literature	this work	literature
[bmim][PF$_6$]	19.91	19.601[18] 19.88[31]	280.03	283.51,[18] 284[27] 285.0,[30] 276.43[31]
[bmim][NTf$_2$]^a	22.43	20.9[32]	267.61	267,[22] 271[27]
[bmim][NTf$_2$]^b	24.53		268.51	270,[32] 271.7[33]

[a] QUILL Centre sample. [b] Covalent Associates sample.

Enthalpy of Fusion. Figure 3 shows the heat flow ϕ versus temperature T curves for the studied samples, while the results for $\Delta_{fus}H$ and T_{fus} are listed in Table 5 together with their reported counterparts. In contrast to the well-behaved curves (i.e., single-peaked) that commonly used organic solvents show, the shape of the curve for [bmim][PF$_6$] is nonregular. Similar behavior was observed by Domanska and Marciniak,[31] who interpreted it as a summary effect of melting and a solid−solid transition. In contrast, Kabo et al.[18] made no reference to this hypothetical solid−solid transition. In any case, the $\Delta_{fus}H$ values from the three sources (note that the reported value from the study of Domanska and Marciniak[31] is the sum of the values corresponding of what they consider two different transitions) are highly consistent (see Table 5). Although the possibility of a solid−solid transition cannot be excluded, the observed agreement could be interpreted on the basis of similar purity levels for the studied samples. In regard to [bmim][NTf$_2$], significant differences have been observed between the $\Delta_{fus}H$ values of the two studied samples. In addition, neither of them agrees with the literature data of Tokuda et al.[32] More significantly, the behavior is markedly different in that the QUILL sample shows a regular, single-peaked ϕ versus T curve, whereas a nonregular curve is observed for the Covalent Associates sample. The single-peaked shape of the curve of the QUILL sample excludes the possibility of a solid−solid transition near melting. The irregularities observed for the Covalent Associates sample can, therefore, be seen as a purity effect. This could be an indication that the nonregular behavior found for [bmim][PF$_6$] comes form impurities too.

Conclusion

This study corroborates that, as a consequence of impurities, the data on the thermodynamic properties of RTILs still lack of the accuracy that those of traditional organic solvents possess. In particular, this work shows that the Cl^- content plays an important role, especially in the case of the density. A more detailed, quantitative analysis of the effect of impurities on thermodynamic properties appears to be highly desirable.

Supporting Information Available:

Additional spreadsheets of density and heat capacity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review May 16, 2006. Accepted June 26, 2006. This research was supported by the Dirección General de Investigación, Ministerio de Ciencia y Tecnología of Spain (Grant BFM2003-09295) and by the Dirección Xeral de Investigación e Desenvolvemento, Xunta de Galicia (Grant PGIDT03DPI38301PR).

JE060222Y