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Thermodynamic properties of 1-alkyl-3-methylimidazolium bromide ionic liquids

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Abstract

Heat capacities and enthalpies of phase transitions for a series of 1-alkyl-3-methylimidazolium bromide ionic liquids have been measured by adiabatic calorimetry. Thermodynamic properties of the compounds were calculated in the temperature range of (5 to 370) K. Water was found to have an additive contribution to the heat capacities of [C_4mim]Br in the liquid state above T_{fus} and in the solid state below 160 K at $w(H_2O) \leqslant 5 \cdot 10^{-3}$.

Keywords: Ionic liquids; Thermodynamic properties; 1-Alkyl-3-methylimidazolium bromides; Synthesis of high-purity ionic liquids

1. Introduction

In recent years, 1-alkyl-3-methylimidazolium ([$C_n$mim]$^+$) ionic liquids (ILs) have been intensively studied [1–9]. [$C_n$mim]X (X = Cl, Br) compounds can be easily used for synthesis of IL with different anions including organic ones [1,5–7,10,11]. That is why [$C_n$mim]Br together with [$C_n$mim]Cl represent a potential source of numerous ILs, and the study of their thermodynamic properties is of great importance.

It is known that [$C_n$mim]Br are very hygroscopic and have low thermal stability in comparison with similar tetrafluoroborate and bis(trifluoromethanesulfonyl)imide ILs [7,10–18]. This makes problems in the preparation of the high-purity samples.

In this work, we report the results of measurements of heat capacities in the temperature range of (5 to 370) K and enthalpies of phase transitions for [$C_n$mim]Br ($C_n = C_2H_5, C_3H_7, C_4H_9$). Thermodynamic properties for ([C_4mim]Br + H_2O) systems are studied as well.

2. Experimental

2.1. Synthesis of ILs

All alkyl bromides and 1-methylimidazole were purchased from Acros Organics. Dry methanol of high purity was obtained from Merck and used as received. ILs investigated in this work were obtained using specially developed method concluding in *N*-methylimidazole quarternization. Such a method based on several procedures [7,10,19] differs from the others in very mild process conditions and solvent addition and results in the formation of high-purity colorless bromide ILs.

2.1.1. 1-Ethyl-3-methylimidazolium bromide [C_2mim]Br

Ethyl bromide was preliminary distilled under inert gas atmosphere over CaH_2, while *N*-methylimidazole was freshly distilled from potassium hydroxide under reduced pressure. Into a round-bottom flask equipped with a magnetic stirrer, a condenser and a $CaCl_2$ tube, 41.8 cm^3 (0.524 mol) of 1-methylimidazole and 70 cm^3 of dry methanol were placed under argon atmosphere. The reaction mass was thoroughly mixed and cooled to $T = (273$ to

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278) K in an ice bath. After 30 min an excess of 1-bromoethane (58.7 cm^3, 0.786 mol) was very slowly added to the intensively stirred reaction mixture. Afterwards the reaction mass was kept at $T = (273$ to $278)$ K for 24 h under stirring and inert atmosphere. Then the temperature was stepwise risen: to $T = 293$ K for 24 h, after this to $T = 313$ K for 24 h and finally to $T = 328$ K for 24 h. *For obtaining colorless IL the maximum temperature should not exceed* $T = 328$ *K.* After the reaction completion methanol and the haloalkane excess were removed by distillation under reduced pressure at $T = 328$ K, the resultant viscous liquid was treated at the same temperature under $p \sim 1$ Pa until it was slowly crystallized. The product is solid at $T = 298$ K and represents colorless crystals. Yield: 97.6 g. Anal. Calc. for $C_6H_{11}N_2Br$ (191.07): C, 0.3772; H, 0.0580; N, 0.1466; Br, 0.4182. Found: C, 0.3776; H, 0.0574; N, 0.1454; Br, 0.4175. Onset loss temperature: 493 K (according to t.g.a. data); ^{1}H n.m.r. (400 MHz, $CDCl_3$): $\delta = 1.44$ (t, 3H, $CH_2\mathit{CH_3}$, J(HH) = 7.32 Hz), 3.95 (s, 3H, NCH_3), 4.25 (m, 2H, $N\mathit{CH_2}CH_3$, J(HH) = 7.9 Hz), 7.53 (s, 1H, H5 (Im)), 7.54 (s, 1H, H4 (Im)), 10.08 (s, 1H, H2 (Im)); i.r. (KBr pellet): 3433 (m), 3138 (m), 3069 (m), 2955 (vs), 2934 (vs), 2857 (s), 1573 (vs), 1464 (s), 1378 (m), 1341 (m), 1172 (s), 1032 (m), 868 (m), 791 (m), 651 (m), 624 (m) cm^{-1}.

2.1.2. 1-Propyl-3-methylimidazolium bromide [C_3mim]Br

1-Propyl-3-methylimidazolium bromide was synthesized in a similar manner as [C_2mim]Br. The obtained product is colorless liquid at $T = 298$ K. Yield: 0.98. Anal. Calc. for $C_7H_{13}N_2Br$ (204.03): C, 0.4099; H, 0.0639; N, 0.1366; Br, 0.3896. Found: C, 0.4391; H, 0.0691; N, 0.1287; Br, 0.3649. Onset loss temperature: 503 K (according to t.g.a. data); ^{1}H n.m.r. (400 MHz, $CDCl_3$): $\delta = 0.77$ (t, 3H, $CH_2CH_2\mathit{CH_3}$, J(HH) = 14.8 Hz), 1.74 (m, 2H, $CH_2\mathit{CH_2}CH_3$, J(HH) = 14.6 Hz), 3.92 (s, 3H, NCH_3), 4.15 (t, 2H, NCH_2, J(HH) = 14.6 Hz), 7.46 (s, 1H, H5 (Im)), 7.55 (s, 1H, H4 (Im)), 10.06 (s, 1H, H2 (Im)); i.r. (KBr pellet): 3437 (m), 3139 (m), 3068 (vs), 2966 (vs), 2877 (m), 1572 (vs), 1461 (s), 1429 (m), 1387 (m), 1345 (m), 1172 (vs), 1090 (m), 864 (m), 801 (m), 755 (m), 651 (m), 6241 (s) cm^{-1}.

2.1.3. 1-Butyl-3-methylimidazolium bromide [C_4mim]Br

This IL was synthesized in accordance with the same procedures as described above and represents colorless crystals at $T = 298$ K. Yield: 0.99. Anal. Calc. for $C_8H_{15}N_2Br$ (219.14): C, 0.4381; H, 0.0684; N, 0.1289; Br, 0.3646. Found: C, 0.4391; H, 0.0691; N, 0.1287; Br, 0.3649. Onset loss temperature: 548 K (according to t.g.a. data); ^{1}H n.m.r. (400 MHz, $CDCl_3$): $\delta = 0.90$ (t, 3H, $CH_2CH_2CH_2\mathit{CH_3}$, J(HH) = 14.7 Hz), 1.34 (m, 2H, $CH_2CH_2\mathit{CH_2}CH_3$, J(HH) = 14.6 Hz), 1.93 (m, 2H, $CH_2\mathit{CH_2}CH_2CH_3$, J(HH) = 14.6 Hz), 4.23 (s, 3H, NCH_3), 4.52 (t, 2H, NCH_2, J(HH) = 14.6 Hz), 8.28 (s, 1H, H5 (Im)), 8.38 (s, 1H, H4 (Im)), 10.02 (s, 1H, H2 (Im)); i.r. (KBr pellet): 3170 (m), 3120 (m), 2980 (m), 2950 (m), 2890 (m), 1580 (s), 1472 (s), 1390 (m), 1350 (m), 1180 (m), 1040 (m), 770 (m) cm^{-1}.

2.2. Sample preparation

Organic impurities were not found in the synthesized samples, with water being the only impurity present in measurable amounts. It was determined that these substances start to decompose after long (30 h) exposition in vacuum of $p \sim 0.1$ Pa at $T = 330$ K. So, the synthesized samples were exposed to vacuum of $p \sim 3$ Pa at $T = 290$ K for a few days and then kept over P_2O_5 for >1 month. The specimens were loaded into containers for calorimetric measurements in a dry box. Molar purities of the samples prepared in such a way were determined by the fractional-melting technique in an adiabatic calorimeter (table 1) with the use of the equation

$$\ln\left(\frac{v}{f}+1\right)=\frac{\Delta_{\mathrm{fus}}H}{RT^2_{\mathrm{fus}}}\Delta T\left(1+\left(\frac{1}{T_{\mathrm{fus}}}-\frac{\Delta C_p}{2\Delta_{\mathrm{fus}}H}\right)\Delta T\right), \qquad (1)$$

where $\Delta T = T_{\mathrm{fus}} - T$; T is an equilibrium temperature corresponding to a melt fraction f; T_{fus} is a triple-point temperature; $\Delta_{\mathrm{fus}}H(T_{\mathrm{fus}})$ is an enthalpy of fusion for a pure compound; ΔC_p is a heat-capacity jump at fusion of a pure compound; v is an amount of impurities in a sample, mole per mole of the main substance. In the calculations only those experimental points were used for which mol fractions of the impurities in a liquid phase were <0.12. The triple-point temperatures for the substances were determined from the data for the purest samples. For the other samples characterized by this technique, only mol fractions of impurities were found from equation (1). Mass fractions of impurities were calculated assuming water to be the main impurity.

To obtain the [C_4mim]Br samples with higher water content a certain amount of water was added to the sample with calorimetrically determined purity. An exact mass of the added water was determined by weighing. To distribute the impurity over the volume the sample was kept in an adiabatic calorimeter at temperatures above T_{fus} for (2 to 3) h.

TABLE 1
Purities of the studied samples

Sample	m/g	$x_{H_2O} \cdot 10^2$	$w_{H_2O} \cdot 10^2$	Procedure
		[C_2mim]Br		
1	0.9821	5.55	0.550	Fractional melting
2	1.0791	2.17	0.209	Fractional melting
		[C_3mim]Br		
3	1.2494			
4	1.1132	6.87	0.644	Fractional melting
5	1.1822	7.50	0.707	Fractional melting
		[C_4mim]Br		
6	0.8756	1.72	0.141	Fractional melting
7	0.9890	5.89	0.482	Fractional melting
8	0.9764	6.24	0.510	Fractional melting
9	0.9857	17.3	1.69	Gravimetric
10	0.9146	38.8	4.95	Gravimetric

The purities of the samples used in the calorimetric measurements are shown in table 1.

2.3. Calorimetric measurements for [C$_n$mim]Br

Heat-capacity measurements were conducted in a Termis BKT-10 adiabatic calorimeter. The calorimeter and the procedure of the measurements have been described elsewhere [20]. The container filled with a substance was evacuated to vacuum of $p \sim 3$ Pa, and then it was filled with helium to $p = 10$ kPa at $T = 290$ K ($p = 10^2$ kPa for samples 9 and 10). Masses of the samples in vacuum are listed in table 1.

After assembling, the measuring system was cooled in a liquid nitrogen bath. If the measurements were performed below 80 K, a liquid helium bath was used. Initial cooling rate of the container with the sample was $\sim$20 mK $\cdot$ s^{-1}. In these cooling conditions liquid [C$_3$mim]Br and [C$_4$mim]Br were supercooled and formed glasses. To obtain crystalline [C$_4$mim]Br, the glass was heated to the temperatures (20 to 30) K above the glass transition temperatures. At these temperatures crystallization was initiated.

It was found that [C$_3$mim]Br forms two crystalline modifications, but cannot be easily crystallized. In an adiabatic calorimeter, the crystals after melting could not be obtained again from the glass and the supercooled liquid. Samples 4 and 5 of [C$_3$mim]Br in the crystal state were loaded in a container, and the purification procedures described above were not applied to them.

To get the completely crystallized samples for all the studied compounds the partly crystallized samples were annealed at temperatures (20 to 30) K below their melting temperatures until spontaneous heat evolution due to crystallization had stopped. The process took less than 15 h.

The experimental heat capacities were corrected with respect to the amount of helium in the container. The differences between C_s and C_p were found to be negligible compared with uncertainty of the measurements.

The triple-point temperatures of the substances were determined by the fractional-melting technique. The enthalpies of fusion for [C$_2$mim]Br and [C$_4$mim]Br were measured in series of special experiments in which an initial temperature, T_{init}, was (40 to 50) K below the fusion temperature, and a final temperature, T_{fin}, was (4 to 16) K above T_{fus}. In the $\Delta_{\mathrm{fus}}H$ calculations T_{init} was adjusted to $T = 295.00$ K with the use of the experimental heat capacities in the corresponding temperature range. Above this temperature heat capacities of the crystals were extrapolated by linear polynomials obtained from the experimental data in the temperature ranges of (270 to 295) K for [C$_2$mim]Br and (271 to 296) K for [C$_4$mim]Br correspondingly. Heat capacities of the liquids were extrapolated to T_{fus} by linear functions obtained from the experimental data in a range of temperatures of (T_{fus} to 370 K).

The glass-transition temperatures, T_g, were determined as the temperatures corresponding to the average values of the heat capacity of the substances in the glass-transition ranges. The heat-capacity jumps, $\Delta_{\mathrm{gl}}^{\mathrm{liq}}C_{\mathrm{s,m}}$, were found as the differences of heat capacities for the metastable liquids and the glasses extrapolated to T_g. The heat-capacity jumps at fusion, $\Delta_{\mathrm{cr}}^{\mathrm{liq}}C_{\mathrm{s,m}}$, were calculated in a similar way.

Heat capacities of [C$_2$mim]Br and [C$_4$mim]Br were extrapolated to $T = 0$ K with the use of the equation $C_p = C_v = aT^3$. The a parameters were calculated by the least-squares fitting of the data in the range of $T = (5$ to $6)$ K. The assumption $C_p = C_v$ was used since $(C_p - C_v)$ has stronger temperature dependence than C_p or C_v have, and normally near $T = 5$ K $(C_p - C_v)$ becomes negligible.

The residual entropy, $\Delta_{\mathrm{cr}}^{\mathrm{gl}}S_{\mathrm{m}}^{\circ}(T \to 0)$, for glass [C$_4$mim]Br was determined as the difference of entropies of the liquid at T_{fus} obtained, on one hand, from the C_p vs T dependence for the crystal and the entropies of phase transitions, and, on the other hand, from the C_p vs T dependence for the glass and the supercooled liquid. The residual enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{gl}}H_{\mathrm{m}}^{\circ}(T \to 0)$ was found in the same manner.

3. Results

3.1. Effect of water on heat capacity for [C$_4$mim]Br

The experimental c_s values for the [C$_4$mim]Br samples with different water content are presented in Tables S.1 and S.2. Effect of water differs in various temperature ranges.

Above T_{fus} specific heat capacity of the samples is a sum of specific heat capacities of IL and liquid water [21]. Maximum deviations between the results for the different samples is $\leqslant 1.2 \cdot 10^{-2} \cdot c_p$ and do not systematically depend on the concentration of water (figure 1). This observation is in agreement with the results for ([C$_4$mim][BF$_4$] + H$_2$O) reported by Rebelo *et al.* [22], and allows one to assume that such an additivity will hold all over the temperature range of existence of the liquid. To apply this below T_{fus} one must know c_p of liquid water down to 220 K. For determination of the heat capacities of water and IL in ([C$_4$mim]Br + H$_2$O) and subsequent calculation of c_p for the pure IL, the following equation was used

$$c_p/\mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{g}^{-1} = w_{\mathrm{IL}}(b_0 + b_1(T/\mathrm{K}) + b_2(T/\mathrm{K})^2) + w_{\mathrm{H_2O}}(b'_0 + b'_1(T/\mathrm{K}) + b'_2/(T/\mathrm{K})^2), \qquad (2)$$

where w_{IL} and $w_{\mathrm{H_2O}}$ are mass fractions of IL and water, b_i are parameters of the equation for the heat capacity of IL, b'_i are parameters of the equation for water. These parameters (table 2) were calculated by the least-squares method using all the experimental points for the liquid samples ([C$_4$mim]Br + H$_2$O). Maximum deviation of the experimental heat capacities from function (2) was $6.7 \cdot 10^{-3} \cdot c_p$. The two approaches give c_p of the pure liquid [C$_4$mim]Br in agreement within $1 \cdot 10^{-3} \cdot c_p$ above T_{fus} for $w_{\mathrm{H_2O}} < 1.7 \cdot 10^{-2}$.

Heat capacities for liquid [C$_4$mim]Br were measured by d.s.c. in a range of temperatures of (298 to 323) K [23].

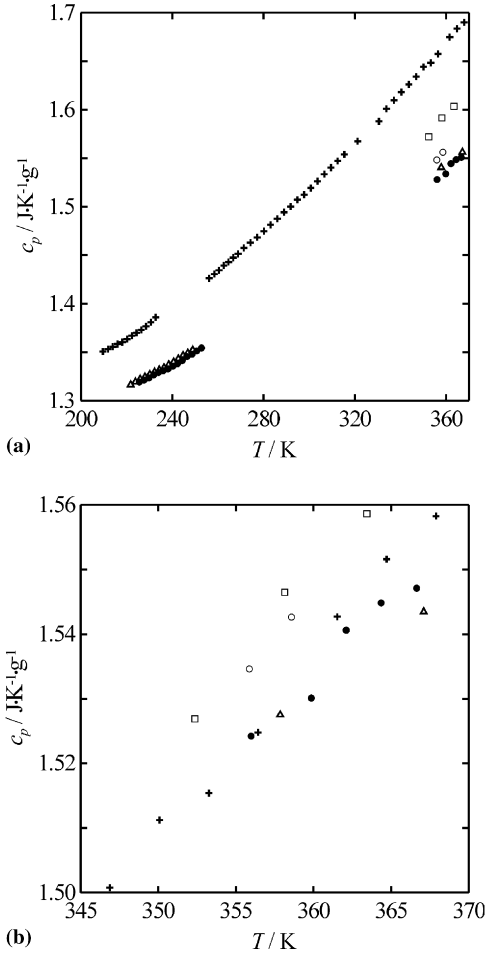

FIGURE 1. Effect of water on heat capacity of liquid [C$_4$mim]Br. Specific heat capacities of (a) samples with water; (b) pure samples calculated assuming $c_p = (1 - w(\mathrm{IL})) \cdot c_p(\mathrm{water}) + w(\mathrm{IL}) \cdot c_p(\mathrm{IL})$. Heat capacities are designated as ● for the sample with water content of $0.14 \cdot 10^{-2}$; △, $0.48 \cdot 10^{-2}$; ○, $0.51 \cdot 10^{-2}$; □, $1.7 \cdot 10^{-2}$; +, $5.0 \cdot 10^{-2}$.

TABLE 2
Parameters of heat-capacity equations for liquid ([C$_4$mim]Br + H$_2$O)

i	b	b'
0	1.186	−2.962
1	$-8.806 \cdot 10^{-5}$	$1.870 \cdot 10^{-2}$
2	$2.935 \cdot 10^{-6}$	$6.159 \cdot 10^{4}$

These results differ from those obtained in this work by $-5 \cdot 10^{-2} \cdot c_p$ at $T = 298$ K and by $0.12 \cdot c_p$ at $T = 323$ K.

The glass-transition range shifts down with increasing water content. Heat capacities of the supercooled liquid could be measured at $T > 225$ K for the purest sample, at $T > 222$ K at water content of $5 \cdot 10^{-3}$, and at $T > 210$ K at water content of $5 \cdot 10^{-2}$ (figure 1).

The effect of water on heat capacity of the crystal is more pronounced than that for the liquid. However, at $w_{\mathrm{H_2O}} \leqslant 5 \cdot 10^{-3}$ the additivity takes place (figure 2). Water has the strongest effect in the pre-melting range $T = (166\ \mathrm{K}\ \text{to}\ T_{\mathrm{fus}})$ (figure 3) where the crystal and the solution ([C$_4$mim]Br + H$_2$O) are in equilibrium. That is

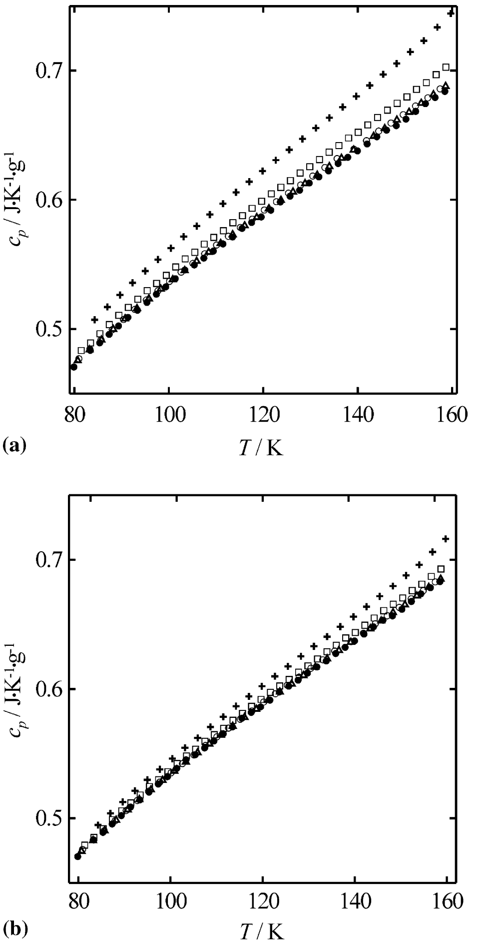

FIGURE 2. Effect of water on heat capacity of crystal [C$_4$mim]Br below 160 K. Specific heat capacities of (a) samples with water; (b) pure samples calculated assuming $c_p = (1 - w(\mathrm{IL})) \cdot c_p(\mathrm{ice}) + w(\mathrm{IL}) \cdot c_p(\mathrm{IL})$. Heat capacities are designated as ● for the sample with water content of $0.14 \cdot 10^{-2}$; △, $0.48 \cdot 10^{-2}$; ○, $0.51 \cdot 10^{-2}$; □, $1.7 \cdot 10^{-2}$; +, $5.0 \cdot 10^{-2}$.

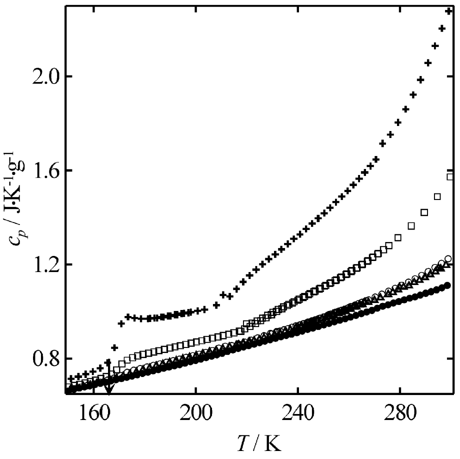

FIGURE 3. Effect of water on heat capacity of crystal [C$_4$mim]Br above 150 K. Heat capacities are designated as ● for the sample with water content of $0.14 \cdot 10^{-2}$; △, $0.48 \cdot 10^{-2}$; ○, $0.51 \cdot 10^{-2}$; □, $1.7 \cdot 10^{-2}$; +, $5.0 \cdot 10^{-2}$.

TABLE 3
Eutectic temperatures for [$C_n$mim]Br

Substance	T_e/K
[C_2mim]Br	170
[C_3mim]Br	
crI	173
crII	165
[C_4mim]Br	166

why it was impossible to check additivity of the heat capacity of the studied system in this range.

As the water content increases the peak with the onset temperature of 166 K and the anomaly in the temperature range of (217 to 274) K become more pronounced. The first peak corresponds to ([C_4mim]Br + H_2O) eutectic. The compositions of the eutectic and the phases forming it are unknown. To determine the compositions the samples with higher water content are to be studied. However, even at the water content of $5 \cdot 10^{-2}$ mass fraction crystallization is problematic. So, we did not study the samples with $w_{H_2O} > 5 \cdot 10^{-2}$.

Water affects the heat capacities of [C_2mim]Br and [C_3mim]Br in the same way. The eutectic temperatures are presented in table 3.

3.2. Thermodynamic properties of [$C_n$mim]Br

[C_2mim]Br forms only crystalline and liquid phases (figure 4, Table S.3). Sample 1 was used for the measurements in the liquid helium range, and sample 2 for those in the liquid nitrogen range (table 1). The experimental enthalpies of fusion are given in table 4, and the fusion temperature, as well as other thermodynamic characteristics for the pure compound including the *a* parameters are presented in table 5. The enthalpy of fusion for the substance from this work essentially exceeds the values of 15.7 $\text{kJ} \cdot \text{mol}^{-1}$ [24] and 15.5 $\text{kJ} \cdot \text{mol}^{-1}$ [25] determined by d.s.c.

An anomaly with $T_{max} = 13$ K occurs in the heat-capacity curve for this compound. The enthalpy and the entropy of the phase transition $\Delta_{trs}H = 3.5 \pm 0.9\ \text{J} \cdot \text{mol}^{-1}$, $\Delta_{trs}S = 0.29 \pm 0.08\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ were determined by numerical integration of the excess C_p and C_p/T in the range of $T = (7$ to $15)$ K. The uncertainties were estimated from the uncertainties of heat-capacity measurements in this temperature range.

[C_3mim]Br forms two crystalline phases. The heat capacities of the phase with higher $T_{fus} = 314.7$ K exceed those for the phase with $T_{fus} = 310.4$ K (figure 5, Table S.4). The purest sample of this compound contains $\sim 6 \cdot 10^{-3}$ mass fraction of water, that causes appearance of anomalies connected with the formation of eutectic ([C_3mim]Br + H_2O) in c_p vs T curve near 170 K. In the determination of the enthalpies of fusion for both crystals the amount of energy required to heat the crystals from T_{init} to T_{fin} was calculated as the total energy spent for heating the samples from $T \sim 169$ K to the temperature above T_{fus} (table 4) in all the consecutive experiments. The heat capacity of the

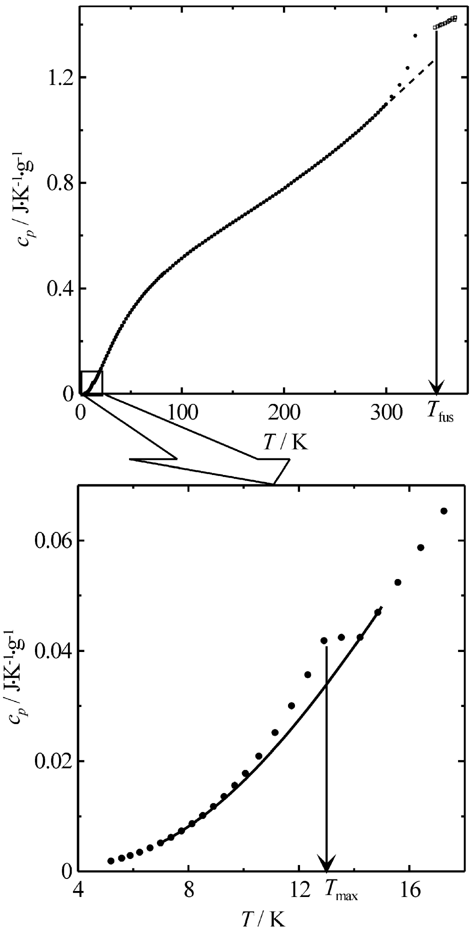

FIGURE 4. Experimental heat capacities for [C_2mim]Br. ● are experimental points for crystal; □, for liquid. Extrapolated heat capacities are shown with a dashed line. A solid line is a baseline for the low-temperature transition.

TABLE 4
Results of determination of enthalpy of fusion for the studied compounds

T_{init}/K	T_{fin}/K	$\Delta_{T_{init}}^{T_{fin}} h$/ $(\text{J} \cdot \text{g}^{-1})$	$\left(\Delta_{T_{init}}^{T_{fus}} h(\text{cr}) + \Delta_{T_{fus}}^{T_{fin}} h(\text{liq})\right)$/ $(\text{J} \cdot \text{g}^{-1})$	$\Delta_{fus}h$/ $(\text{J} \cdot \text{g}^{-1})$
		[C_2mim]Br (sample 2)		
295.00	355.68	168.81	72.67	96.14
295.00	366.09	184.02	87.39	96.63
295.00	358.73	173.27	76.95	96.32
			$\langle \Delta_{fus}h \rangle / (\text{J} \cdot \text{g}^{-1})$	96.36 ± 0.62
		Crystal I [C_3mim]Br (sample 4)		
168.85	313.73	198.24	130.36	67.88
		Crystal II [C_3mim]Br (sample 5)		
169.59	313.48	235.36	129.12	106.24
		[C_4mim]Br (sample 6)		
295.00	355.22	179.35	74.46	104.89
295.00	355.63	179.61	74.73	104.89
295.00	355.49	179.53	74.49	105.04
			$\langle \Delta_{fus}h \rangle / (\text{J} \cdot \text{g}^{-1})$	104.94 ± 0.21

TABLE 5
Thermodynamic characteristics of [C$_n$mim]Br

	[C$_2$mim]Br	[C$_3$mim]Br		[C$_4$mim]Br
	Crystal	Crystal I	Crystal II	Crystal
$a \cdot 10^3/(\mathrm{J \cdot K^{-4} \cdot mol^{-1}})$	2.61			4.85
T_{fus}/K	349.91	314.7	310.4	351.35
$\Delta_{\mathrm{fus}}H^\circ_{\mathrm{m}}(T_{\mathrm{fus}})/(\mathrm{kJ \cdot mol^{-1}})$	18.26 ± 0.12	13.5	21.4	22.88 ± 0.05
$\Delta_{\mathrm{fus}}S^\circ_{\mathrm{m}}(T_{\mathrm{fus}})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	52.62 ± 0.34	42.8	68.8	65.12 ± 0.13
$\Delta^{\mathrm{liq}}_{\mathrm{cr}}C^\circ_{p,\mathrm{m}}(T_{\mathrm{fus}})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	21.7 ± 1.8	64	67	51.8 ± 2.2
$C^\circ_{p,\mathrm{m}}(298.15\ \mathrm{K})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	207.5 ± 0.8			241.6 ± 1.0
$S^\circ_{\mathrm{m}}(298.15\ \mathrm{K})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	248.7 ± 1.1			300.3 ± 1.3
$\Delta_0^{298}H^\circ_{\mathrm{m}}/(\mathrm{kJ \cdot mol^{-1}})$	35.04 ± 0.16			41.39 ± 0.19
		Glass		
$a \cdot 10^3/(\mathrm{J \cdot K^{-4} \cdot mol^{-1}})$				8.74
T_{g}/K		209		218.9
$\Delta^{\mathrm{liq}}_{\mathrm{gl}}C^\circ_{p,\mathrm{m}}(T_{\mathrm{g}})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$		81 ± 2		84.2 ± 1.4
$\Delta^{\mathrm{gl}}_{\mathrm{cr}}S^\circ_{\mathrm{m}}(T \to 0)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$				16.6 ± 2.5
$\Delta^{\mathrm{gl}}_{\mathrm{cr}}H^\circ_{\mathrm{m}}(T \to 0)/(\mathrm{kJ \cdot mol^{-1}})$				11.3 ± 0.5
		Liquid at $T = 360$ K		
$C^\circ_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	268.6 ± 1.1	299.7 ± 1.2		336.4 ± 1.3
$S^\circ_{\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	344.2 ± 1.5			416.4 ± 1.9
$\Delta_0^{360}H^\circ_{\mathrm{m}}/(\mathrm{kJ \cdot mol^{-1}})$	67.56 ± 0.30			81.07 ± 0.36

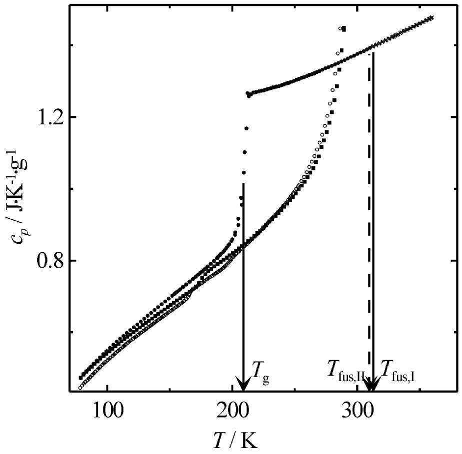

FIGURE 5. Experimental heat capacities for [C$_3$mim]Br, where ■ are heat capacities for crystal I; ○, for crystal II; ●, for glass and supercooled liquid; ×, for liquid.

crystals was extrapolated to T_{fus} with linear equations obtained from the experimental data in a range of temperatures of (120 to 170) K for crystal I and (130 to 170) K for crystal II. It is impossible to compare the present results with the obtained earlier value [24] $\Delta_{\mathrm{fus}}H(32.8\ °\mathrm{C}) = 16.3\ \mathrm{kJ \cdot mol^{-1}}$ since in the cited paper the crystal modification of the compound was not specified.

At cooling the liquid forms glass with the characteristics presented in table 5. Measurements of heat capacity for the supercooled liquid were possible all over the temperature range of (T_{g} to T_{fus}) K.

[C$_4$mim]Br forms one crystalline phase, glass, and liquid (figure 6, Table S.1). The experimental results on the $\Delta_{\mathrm{fus}}H$ determination are shown in table 4. The fusion temperature and the other thermodynamic parameters for the pure

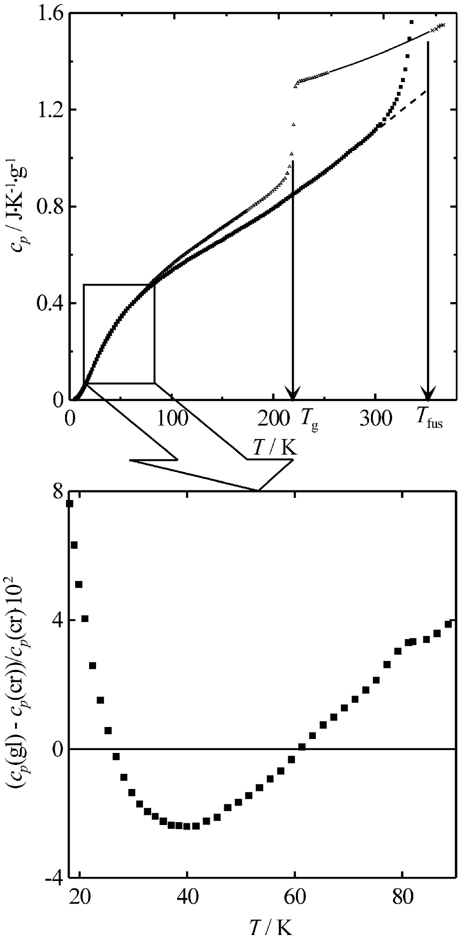

FIGURE 6. Experimental heat capacities for [C$_4$mim]Br, where ■ are heat capacities of crystal; △, for glass and supercooled liquid; ×, for liquid. Extrapolated heat capacities are shown with a dashed line. A solid line designates interpolated heat capacities for supercooled liquid.

compound are presented in table 4. The results on $\Delta_{\mathrm{fus}}H$ from [24] are underestimated by $0.24 \cdot \Delta_{\mathrm{fus}}H$ compared with the present data.

The characteristics of glass [C$_4$mim]Br are presented in table 5. The heat capacities of the glass in the temperature range of (25 to 60) K lie below those for the crystal (figure 6). This is unusual for organic compounds since normally heat capacities for glass exceeds those for crystal all over the temperature range of their existence. The residual entropy for the glass [C$_4$mim]Br is rather low (table 4), which is evidence of high degree of ions' ordering in

TABLE 6
Thermodynamic properties for [C$_2$mim]Br

T/K	$C^\circ_{p,\mathrm{m}}/R$	S°_m/R	$\Delta_0^T H^\circ_\mathrm{m}/RT$	$-\Delta_0^T G^\circ_\mathrm{m}/RT$
		Crystal		
0	0	0	0	0
5	0.0387	0.0131	0.0098	0.0033
10	0.4012	0.1202	0.0920	0.0282
15	1.103	0.433	0.327	0.106
20	2.022	0.873	0.633	0.240
25	3.007	1.430	1.009	0.421
30	3.979	2.065	1.424	0.641
35	4.893	2.748	1.855	0.893
40	5.717	3.456	2.287	1.169
45	6.467	4.173	2.710	1.463
50	7.155	4.891	3.121	1.770
60	8.367	6.306	3.897	2.408
70	9.385	7.674	4.611	3.063
80	10.28	8.987	5.265	3.722
90	11.08	10.25	5.868	4.378
100	11.80	11.45	6.425	5.025
110	12.48	12.61	6.945	5.662
120	13.12	13.72	7.433	6.288
130	13.73	14.80	7.894	6.901
140	14.33	15.84	8.333	7.502
150	14.92	16.84	8.753	8.092
160	15.50	17.83	9.156	8.670
170	16.08	18.78	9.547	9.236
180	16.67	19.72	9.926	9.793
190	17.27	20.64	10.30	10.34
200	17.88	21.54	10.66	10.88
210	18.51	22.42	11.02	11.41
220	19.15	23.30	11.37	11.93
230	19.81	24.17	11.73	12.44
240	20.49	25.02	12.08	12.95
250	21.19	25.87	12.43	13.45
260	21.91	26.72	12.78	13.94
270	22.65	27.56	13.13	14.43
280	23.46	28.40	13.48	14.91
290	24.29	29.23	13.84	15.39
298.15	24.96	29.92	14.14	15.78
300	25.11	30.07	14.20	15.87
310	25.94	30.91	14.57	16.34
320	26.76	31.75	14.94	16.81
330	27.59	32.58	15.31	17.27
340	28.42	33.42	15.68	17.74
349.92	29.24	34.25	16.05	18.19
		Liquid		
349.92	31.85	40.52	22.33	18.19
350	31.85	40.53	22.33	18.20
360	32.31	41.43	22.60	18.83
370	32.76	42.33	22.87	19.45

TABLE 7
Thermodynamic properties of [C$_4$mim]Br

T/K	$C^\circ_{p,\mathrm{m}}/R$	S°_m/R	$\Delta_0^T H^\circ_\mathrm{m}/RT$	$-\Delta_0^T G^\circ_\mathrm{m}/RT$
		Crystal		
0	0	0	0	0
5	0.0714	0.0243	0.0182	0.0061
10	0.601	0.205	0.154	0.0506
15	1.581	0.623	0.457	0.165
20	2.793	1.241	0.8872	0.353
25	4.054	2.000	1.395	0.605
30	5.267	2.847	1.940	0.907
35	6.371	3.744	2.496	1.248
40	7.348	4.660	3.043	1.617
45	8.219	5.576	3.570	2.006
50	8.998	6.483	4.075	2.409
60	10.33	8.246	5.010	3.236
70	11.45	9.925	5.852	4.072
80	12.42	11.52	6.614	4.904
90	13.29	13.03	7.309	5.724
100	14.08	14.47	7.947	6.528
110	14.81	15.85	8.538	7.313
120	15.49	17.17	9.089	8.080
130	16.15	18.43	9.607	8.828
140	16.80	19.66	10.10	9.558
150	17.45	20.84	10.57	10.27
160	18.10	21.98	11.02	10.97
170	18.76	23.10	11.45	11.65
180	19.44	24.19	11.88	12.32
190	20.13	25.26	12.29	12.97
200	20.86	26.31	12.70	13.61
210	21.64	27.35	13.11	14.24
220	22.44	28.37	13.52	14.86
230	23.22	29.39	13.92	15.47
240	23.99	30.39	14.32	16.07
250	24.80	31.39	14.73	16.66
260	25.64	32.38	15.13	17.25
270	26.56	33.36	15.54	17.83
280	27.47	34.35	15.95	18.40
290	28.36	35.33	16.36	18.97
298.15	29.08	36.12	16.70	19.42
300	29.24	36.30	16.77	19.53
310	30.12	37.28	17.19	20.08
320	31.01	38.25	17.61	20.64
330	31.89	39.21	18.03	21.18
340	32.77	40.18	18.45	21.73
350	33.65	41.14	18.87	22.27
351.35	33.77	41.27	18.93	22.34
		Liquid		
351.35	40.00	49.10	26.76	22.34
360	40.45	50.08	27.08	23.00
370	41.00	51.20	27.45	23.74
		Glass		
0	0	1.999		
5	0.136	2.043	272.5	−270.4
10	0.820	2.314	136.5	−134.1
15	1.798	2.827	91.4	−88.6
20	2.934	3.498	69.1	−65.6
25	4.086	4.277	56.01	−51.74
30	5.193	5.121	47.45	−42.33
35	6.229	6.000	41.49	−35.49
40	7.174	6.894	37.14	−30.25
45	8.042	7.790	33.86	−26.07
50	8.849	8.680	31.32	−22.64
60	10.31	10.43	27.70	−17.27
70	11.61	12.11	25.31	−13.20

TABLE 7 (*continued*)

T/K	$C^\circ_{p,\mathrm{m}}/R$	S°_m/R	$\Delta_0^T H^\circ_\mathrm{m}/RT$	$-\Delta_0^T G^\circ_\mathrm{m}/RT$
80	12.79	13.74	23.67	−9.93
90	13.83	15.31	22.52	−7.21
100	14.78	16.82	21.70	−4.88
110	15.67	18.27	21.11	−2.84
120	16.50	19.67	20.70	−1.03
130	17.29	21.02	20.40	0.62
140	18.06	22.33	20.21	2.12
150	18.82	23.60	20.09	3.51
160	19.59	24.84	20.04	4.81
170	20.36	26.05	20.03	6.02
180	21.14	27.24	20.07	7.17
190	21.96	28.40	20.15	8.25
200	22.83	29.56	20.27	9.29
210	23.98	30.70	20.42	10.28
220	30.52	31.89	20.65	11.24
230	34.82	33.41	21.24	12.17
240	35.16	34.90	21.81	13.08
250	35.52	36.34	22.36	13.99
260	35.89	37.74	22.87	14.87
270	36.28	39.10	23.36	15.74
280	36.68	40.43	23.83	16.60
290	37.10	41.72	24.28	17.45
298.15	37.45	42.76	24.63	18.12
300	37.53	42.99	24.71	18.28
310	37.98	44.23	25.13	19.09
320	38.44	45.44	25.54	19.90
330	38.92	46.63	25.94	20.69
340	39.42	47.80	26.33	21.47
350	39.93	48.95	26.71	22.24
351.35	40.00	49.10	26.76	22.34

the glass. The glass transition temperature is 0.69 T_fus, which is in agreement with the empirical correlation $T_\mathrm{g}/T_\mathrm{fus} \approx 2/3$.

A very small anomaly with the maximum temperature of $T_\mathrm{max} = 11$ K and $\Delta H = 0.9 \pm 0.7\ \mathrm{J \cdot mol^{-1}}$ was observed in the glass. It is not clear if the anomaly is related with the nature of the compound or with the uncertainty in the measurements. That is why it was not taken into account in calculation of the thermodynamic functions.

The additivity found for ([C$_4$mim]Br + H$_2$O) at water content of $\leqslant 5 \cdot 10^{-3}$ allowed us to calculate the thermodynamic properties for pure [C$_4$mim]Br and [C$_2$mim]Br (tables 6 and 7). The difference between the entropies of liquid [C$_4$mim]Br and [C$_2$mim]Br is 72 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at $T = 360$ K. This value is lower than the average increment per two CH$_2$-groups in the series of normal alkanes C$_{14}$–C$_{16}$–C$_{18}$ $2\Delta_{\mathrm{CH_2}}S = 76.7\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ calculated from the thermodynamic tables [26]. The difference in the heat capacities of the mentioned ILs is 67 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and is comparable with the similar value $2\Delta_{\mathrm{CH_2}}C_p = 68\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for *n*-alkanes.

[C$_4$mim]Cl forms two crystals. The alkyl chain in the cation is in a *gauche* conformation in one crystal, and in a *trans* conformation in the other [27]. Only the [C$_4$mim]Br crystal with *gauche* conformation of the alkyl chain is stable [27]. The temperature dependence of the heat capacity for crystal I of [C$_3$mim]Br is similar to that for the [C$_4$mim]Br crystal. One may speculate that the structures of the two crystals are also similar. However, the enthalpy of fusion for crystal I [C$_3$mim]Br is essentially lower than that for crystal II. This can serve as the evidence of lower stability of crystal I.

4. Conclusions

In this work heat capacities and enthalpies of phase transitions were measured for three 1-alkyl-3-methylimidazolium bromides. Thermodynamic properties of these compounds were calculated from these data. It was found that the ability to vitrify and to crystallize among the studied ILs strongly depends on the length of the alkyl chain in the imidazolium ring. Along with this, it was concluded from the measurements in the ([C$_4$mim]Br + H$_2$O) system that at concentrations of water $<5 \cdot 10^{-3}$ mas. the equation $c_p = c_p(\text{water}) + c_p(\text{IL})$ describes c_p within $1 \cdot 10^{-3} \cdot c_p$ for the liquid above T_fus and the crystal below 160 K.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2006.05.008.

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