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Heat Capacity of Ionic Liquids: Experimental Determination and Correlations with Molar Volume

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The heat capacities of nine room-temperature ionic liquids (ILs) were measured in an adiabatic calorimeter. The obtained results were compared with the literature data. It was demonstrated that in most works the uncertainty of the heat capacity measurements for ILs is underestimated, and the possible causes of this were discussed. With the use of the set of 19 ILs for which the reliable heat capacity data and the density data are available, it was found that the quotient of heat capacity at constant pressure to volume for these liquids remains constant within ± 5 % at a given temperature and linearly changes with temperature in the temperature range of (258 to 370) K. It was demonstrated that the selection of an IL for technical applications is limited not by its heat capacity but by the other parameters.

Introduction

The importance of some very simple relationships in physical chemistry is well-known. The constancy of heat capacity of the crystals with the simple crystal structure $C_p \approx 3R$ (Dulong−Petit law) and the constancy of vaporization entropy at the normal boiling point $\Delta_{\mathrm{vap}}S \approx$ const (Trouton's rule) can serve as examples. Now it is clear that these relationships are valid under certain conditions. For the Dulong−Petit law, the condition of $T > h\nu_{\mathrm{lat}}/k_{\mathrm{B}}$ is necessary where ν_{lat} is the maximum frequency of lattice vibrations. The Trouton's rule works well for the nonassociated liquids and vapors.

For technical applications of room-temperature ionic liquids (ILs) as heat accumulators, heat carriers, reaction media, and so forth, not molar C_p but specific $c_p = C_p/M$ and the volumic C_p/V heat capacities are important. It was demonstrated in refs 1 and 2 that simple linear correlations of the molar heat capacity with the molar volume hold for ILs at $T = 298.15$ K. In ref 1, we obtained the following equation for the set of 15 ILs:

$$C_p = A(V - 2.56\cdot 10^{-4}) + B \tag{1}$$

where C_p is the molar heat capacity of the liquid, $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, V is the molar volume of the liquid, $\mathrm{m^3\cdot mol^{-1}}$, $A = (1.75 \pm 0.05)\cdot 10^6$, and $B = (4.85 \pm 0.04)\cdot 10^2$. Gardas and Coutinho[2] noted the constancy of the volumic heat capacity at $T = 298.15$ K for the set of 18 ILs. However, it should be noted that, according to the data of Table 3 from ref 2, the average value should be $C_p/V = 1.937 \pm 0.045\ \mathrm{J\cdot K^{-1}\cdot cm^{-3}}$, but not $C_p/V = 1.9516 \pm 0.0090\ \mathrm{J\cdot K^{-1}\cdot cm^{-3}}$ as stated in the original paper. The limited sets of ILs were used in both the works. In addition, the uncertainties of the heat capacity values used for both correlations were up to ± 10 %. So, it is impossible to find out whether the deviations of the experimental data from the predictions are due to quality of the data or are inherent in the correlations.

In this work we report the results of the heat capacity measurements in an adiabatic calorimeter for nine ILs with different cations and anions. Using the results of this work and the reliable literature data, the molar heat capacity of ILs was correlated with the molar volume over the wide temperature range.

Experimental Section

The characteristics of the IL samples used in this study are presented in Table 1. The samples of [C_3mim]Br and [C_{14}mim]NTf_2 were provided by Prof. Ya. S. Vygodskii; the other samples were the commercial ones. The procedure of preparation of the samples with the NTf_2^- and OTf^- anions was similar to that in ref 3 and included exposition to a vacuum of 10^{-3} Pa for several days at temperatures increasing stepwise from (290 to 373) K. This procedure was not applied to the other samples to avoid their decomposition in vacuum. The [C_3mim]Br sample was kept over P_2O_5 for a few weeks for drying. The purity and the triple-point temperature T_{fus} of most ILs were determined by the fractional-melting technique in an adiabatic calorimeter (Table 1). The fusion enthalpies required for this determination were also obtained by adiabatic calorimetry. It was impossible to crystallize [C_2mim]$EtSO_4$ and [C_4mim]BF_4 in the calorimeter. The purity of these compounds stated by supplier is reported in Table 1.

The heat capacities of ILs were measured with an uncertainty of ± 0.4 % in the TAU-10 adiabatic calorimeter. The calorimeter and the experimental procedures were described in ref 4. The heat capacities of the [$C_n$mim]NTf_2 ILs obtained earlier with this calorimeter[3−5] agree with the results[6−8] also obtained in an adiabatic calorimeter within ± 0.45 % that confirms the reliability of our calorimeter. The masses of the samples are presented in Table 1.

The procedure of density measurements for ILs was described earlier.[9] The uncertainty in the densities is estimated to be ± 2 $\mathrm{kg\cdot m^{-3}}$.

Results and Discussion

The obtained experimental heat capacities of ILs are presented in Figure 1 and in the Supporting Information. The

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Table 1. Characteristics of the Used IL Samples

name	designation	M / g·mol^{-1}	100 x_1	T_{fus} / K	$\Delta_{fus}H$ / kJ·mol^{-1}	m_{sample} / g
1-ethyl-3-methylimidazolium ethylsufate	[C_2mim]$EtSO_4$	236.29	>99[a]	N/A	N/A	0.9887
1-methyl-3-propylimidazolium bromide	[C_3mim]Br	205.10	98.8	309.56 ± 0.03	19.2 ± 0.1	0.9719
1-butyl-3-methylimidazolium dicyanamide	[C_4mim]$N(CN)_2$	205.26	97.8	270.83 ± 0.02	17.8 ± 0.1	0.9325
1-butyl-3-methylimidazolium tetrafluoroborate	[C_4mim]BF_4	226.02	>99[a]	N/A	N/A	1.0248
1-butyl-3-methylimidazolium trifluoromethanesulonate	[C_4mim]OTf	288.29	99.6	290.98 ± 0.01	19.4 ± 0.1	0.9922
1-methyl-3-octylimidazolium tetrafluoroborate	[C_8mim]BF_4	282.13	99.4	245.75 ± 0.01	14.7 ± 0.1	0.9481
1-methyl-3-tetradecylimidazolium bis(trifluoromethanesulfonyl)imide	[C_{14}mim]NTf_2	559.63	98.6	308.72 ± 0.04	39.9 ± 0.1	0.6503
butyltrimethylammonium bis(trifluoromethanesulfonyl)imide	[$BuMe_3N$]NTf_2	396.37	99.8	290.23 ± 0.02	11.4 ± 0.1	1.1131
1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	[C_4MePrl]NTf_2	422.41	99.8	265.65 ± 0.05	21.9 ± 0.1	0.8403

[a] Mass fraction stated by supplier.

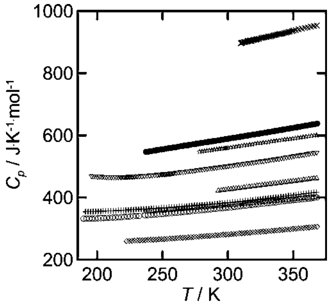

Figure 1. Heat capacity of the studied ILs: +, [C_2mim]$EtSO_4$; ◊, [C_3mim]Br; □, [C_4mim]$N(CN)_2$; ○, [C_4mim]BF_4; △, [C_4mim]OTf; ▽, [C_8mim]BF_4; ×, [C_{14}mim]NTf_2; ★, [$BuMe_3N$]NTf_2; ●, [C_4MePrl]NTf_2.

observed $C_p(T)$ dependences were described by the polynomials:

$$C_p/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = A_0 + A_1\left(\frac{T}{100\ \mathrm{K}}\right) + A_2\left(\frac{T}{100\ \mathrm{K}}\right)^2 + A_3\left(\frac{T}{100\ \mathrm{K}}\right)^3 \quad (2)$$

The polynomial coefficients and the heat capacities at T = 298.15 K are reported in Table 2.

Comparison with Literature. [C_2mim]$EtSO_4$. The heat capacity of [C_2mim]$EtSO_4$ was measured by adiabatic calorimetry in refs 10 and 11 and by differential scanning calorimetry (DSC) in refs 12 to 16. The deviation of the literature data from the present results is demonstrated in Figure 2. The heat capacities by Zhang et al.[10] are (0.7 to 5.7) % lower than those obtained in this work, and the minimal deviation is observed near T = 260 K. At the same time, the results of the other paper from that group[11] are systematically too high by (5.5 to 7.0) %. Taking into account that the comparable difference is also observed for [C_4mim]BF_4,[17] one can suppose that the errors in refs 10 and 11 are related to the calorimeter or the experimental procedure but not to the sample quality.

The largest deviation from the results of this work reaches 41 %.[12] The cause of such a large deviation is unknown. The results by Yu et al.[13] are systematically overestimated by (12 to 13) %. This is probably related to the quality of the sample used in the cited work. In similar measurements for the other ILs made by those authors[18] the deviation from the results of adiabatic calorimetry did not exceed 3.2 %, which is above the stated uncertainty of ± 2 %, but still much lower than that for [C_2mim]$EtSO_4$. The stated uncertainty in ref 15 is ± 0.3 %, but the deviation from the results of adiabatic calorimetry is about 3 %. The discrepancy between the results in ref 14 and the results of this work does not exceed the stated uncertainty of ± 5 % below 340 K; however, at higher temperatures, the discrepancy increases by almost two times and reaches 9 %. The deviation of the results[16] does not exceed the stated uncertainty of measurements of ± 4 %.

[C_3mim]Br. We have measured heat capacity of this IL by adiabatic calorimetry[19] using the sample with the significant water content (mole fraction of 7 %). The difference of these results with the ones from the present work is about 1 %.

[C_4mim]$N(CN)_2$. The values of heat capacity of [C_4mim]$N(CN)_2$ determined earlier by DSC in the temperature range of (298 to 327) K[20] are (3 to 4) % lower than the values presented in this work, which slightly exceeds the uncertainty of ± 3 % stated by the authors.[20]

[C_4mim]BF_4. The heat capacity of this IL was reported in the largest number of works.[17,18,20−26] The DSC method was used in all of them except for ref 17 where the method of adiabatic calorimetry was used. The deviations from the values obtained in this work are presented in Figure 3. The results of refs 18, 22, and 23 and the ones obtained in this work are within the combined uncertainty of the measurements and agree within ± 1 %. The C_p values from ref 26 are lower than the ones from this work by (0.9 to 1.4) %, which exceeds the stated uncertainty of ± 0.3 %. A good agreement of the results from a number of works allows us to assume that the results[17] obtained by adiabatic calorimetry contain the systematic error. The deviation of the results[17,20,21,24] significantly exceeds the stated uncertainties and is above 10 % in case of refs 21 and 24.

[C_4mim]OTf. The heat capacity of [C_4mim]OTf was studied by DSC in refs 14, 15, 18, 20, and 27. The deviations of those results from the values obtained in this work are presented in Figure 4. The heat capacities[15] differ from those obtained here by less than 0.8 %. The measurements[27] were performed with the use of different calorimetric methods. The deviation from the results of this work does not exceed 3 % which agrees with the stated uncertainty of the measurements of ± 5 %. The deviation of the results[18,20] does not exceed 4.3 %. These results[14] have the largest deviation (to 10 %).

Table 2. Coefficients of Polynomials (2) for the Studied ILs

compound	T range K	A_0	A_1	A_2	A_3	$C_{p,298}$ $J\cdot K^{-1}\cdot mol^{-1}$
$[C_2mim]EtSO_4$	190 to 290	512.78	−215.22	90.370	−11.040	
	290 to 370	339.72	−13.868	9.4959		382.8
$[C_3mim]Br$	222 to 370	276.13	−44.242	20.187	−1.6190	280.8
$[C_4mim]N(CN)_2$	235 to 370	405.60	−86.008	35.223	−3.2648	375.7
$[C_4mim]BF_4$	189 to 302	482.37	−204.34	83.844	−9.4857	367.1
	302 to 370	225.26	47.490			
$[C_4mim]OTf$	291 to 370	298.11	35.004	2.8361		427.7
$[C_8mim]BF_4$	195 to 250	1612.0	−1418.5	572.19	−74.840	
	250 to 370	411.85	0	9.6708		497.8
$[C_{14}mim]NTf_2$	309 to 370	595.16	97.520			885.9[a]
$[BuMe_3N]NTf_2$	277 to 370	380.98	59.821			559.3
$[C_4MePrl]NTf_2$	236 to 370	276.21	184.52	−41.185	4.8196	588.0

[a] Extrapolated.

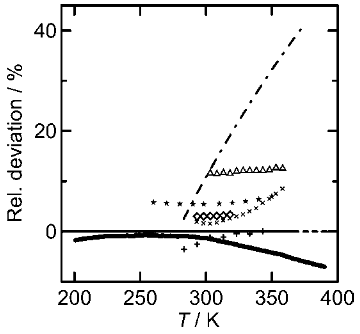

Figure 2. Comparison of literature heat capacities of $[C_2mim]EtSO_4$ with those obtained in this work: ●, ref 10; ★, ref 11; -•-, ref 12; △, ref 13; ×, ref 14; ◇, ref 15; +, ref 16.

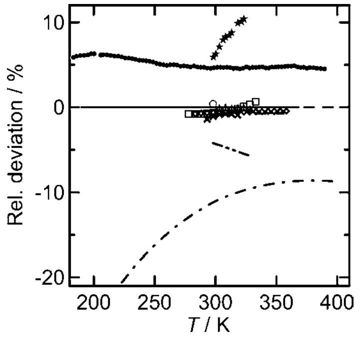

Figure 3. Comparison of literature heat capacities of $[C_4mim]BF_4$ with those obtained in this work: ●, ref 17; ▽, ref 18; -••-, ref 20; -•-, ref 21; ◇, ref 22; □, ref 23; ★, ref 24; ○, ref 25; ×, ref 26.

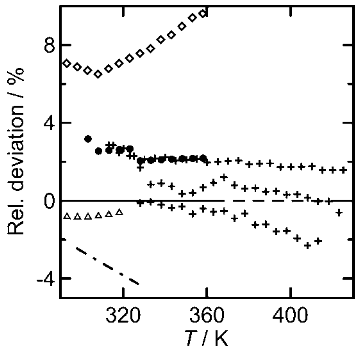

Figure 4. Comparison of literature heat capacities of $[C_4mim]OTf$ with those obtained in this work: ◇, ref 14; △, ref 15; ●, ref 18; -•-, ref 20; +, ref 27.

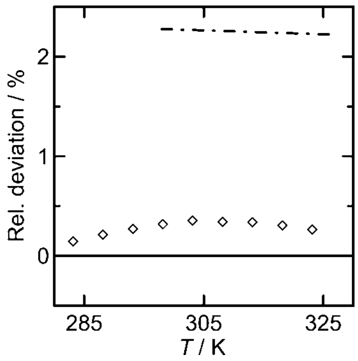

Figure 5. Comparison of literature heat capacities of $[C_8mim]BF_4$ with those obtained in this work: ◇, ref 22; -•-, ref 28.

$[C_8mim]BF_4$. The heat capacities of this IL measured by DSC in ref 22 agree with the results of this work within 0.5 % (Figure 5). The difference with the results[28] does not exceed 2.5 %. In both cases, the deviations agree with the stated uncertainty of the measurements.

$[C_4MePrl]NTf_2$. The heat capacity of $[C_4MePrl]NTf_2$ was measured by DSC in refs 14 and 29. The results from ref 14 are too high by (5.0 to 8.1) % and those from ref 29 by (1.5 to 5.0) % (Figure 6).

Thus, the real uncertainty of the measurements exceeds the estimated uncertainty reported by the authors in most cases. When reporting the data on heat capacity of ILs, the authors should probably pay more attention to checking the performance of their calorimeters. At present, the reliable heat capacity data are available for many ILs and can be used both for checking and calibration of the calorimeters. For example, the heat capacity of $[C_6mim]NTf_2$ was measured in adiabatic calorimeters by Blokhin et al.[4] and Shimizu et al.[8] as a part of the IUPAC project.[30] The recommended values of the $[C_6mim]NTf_2$ heat capacity are presented in ref 31.

One more source of error in the measurements can be impurities in the studied samples. At a low concentration of impurities, the specific heat capacity of a sample can be calculated as a sum of specific heat capacities of individual components multiplied by their mass fractions. The possible impurities in ILs were specified in ref 32. Table 3 describes the effect of 0.01 mass fraction of these impurities on the specific heat capacity of a sample of $[C_4mim]BF_4$. This level of impurities is typical for the best commercially available samples. In most cases, the effect of impurities is comparable to the uncertainty of the most accurate heat capacity values. The only compound which shifts the heat capacity of the sample significantly is water. The sample can absorb water when being loaded into the calorimeter on air. This is especially important for small samples. Absorption of water can be a possible explanation of the fact that most heat capacity values from literature are too high compared to the results of this work.

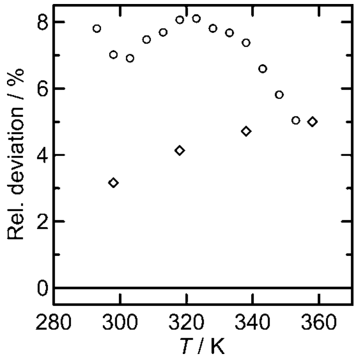

Figure 6. Comparison of literature heat capacities of [C_4MePrl]NTf_2 with those obtained in this work: ○, ref 14; ◇, ref 29.

Table 3. Effect of 0.01 Mass Fraction of Impurity on the Specific Heat Capacity of [C_4mim]BF_4 at $T = 298$ K

impurity	c_p/J·K^{-1}·g^{-1} [a]	$\frac{100\Delta c_p([C_4mim]BF_4)}{c_p([C_4mim]BF_4)}$
[C_4mim]Cl	1.815[b]	0.1
[C_4mim]Br	1.421[c]	−0.1
1-bromobutane	1.185[d]	−0.3
1-chlorobutane	1.720	0.1
1-methylimidazole	1.794[d]	0.1
sodium tetrafluoroborate	1.095[e]	−0.3
water	4.189	1.6
acetonitrile	2.233	0.4
acetone	2.191	0.3
ethyl acetate	1.904	0.2
toluene	1.706	0.1
1,1,1-trichloroethane	1.321	−0.2
methanol	2.533	0.6
dichloromethane	1.189	−0.3
trichloromethane	0.954	−0.4

[a] Evaluated values from ref 39 unless otherwise noted. [b] Ref 33. [c] Ref 19. [d] Ref 34. [e] Solid-phase data from ref 35.

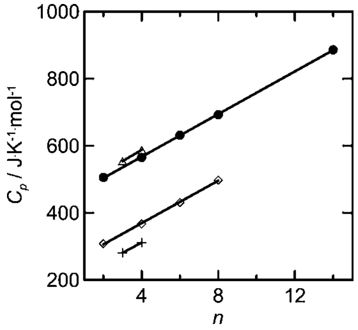

Figure 7. Trends in heat capacity of ILs at $T = 298.15$ K: +, [$C_n$mim]Br; ◇, [$C_n$mim]BF_4; ●, [$C_n$mim]NTf_2; △, [C_nMePrl]NTf_2.

Regularities in Heat Capacity in a Homologous Series of ILs. The regularities of the heat capacity at $T = 298.15$ K in the homologous series of ILs are demonstrated in Figure 7. The heat capacities obtained in this work as well as the literature data with the uncertainty of better than ± 1 % were used in this plot: for [$C_n$mim]NTf_2, $n = 2$,[3,6] 4,[5−7,36] 6,[4,8] and 8;[3] for [$C_n$mim]BF_4, $n = 2$[2] and 6;[37] for [C_4mim]Br;[19] for [C_3MePrl]-NTf_2.[22] The contribution per CH_2-group is 30.6 ± 1.7 J·K^{-1}·mol^{-1} for [$C_n$mim]Br, 31.7 ± 1.2 J·K^{-1}·mol^{-1} for [$C_n$mim]BF_4, 31.8 ± 0.4 J·K^{-1}·mol^{-1} for [$C_n$mim]NTf_2, and 34.0 ± 6.0 J·K^{-1}·mol^{-1} for [C_nMePrl]NTf_2. All of the values agree within their uncertainties, and the weighted average value is $\Delta C_p(H \rightarrow CH_3) = 31.7 \pm 0.4$ J·K^{-1}·mol^{-1}. The deviation from the additive lines in the [$C_n$mim]NTf_2 and [$C_n$mim]BF_4 series do not exceed ± 0.7 %. The additivity in the homologous series of ILs can be used for checking of the mutual consistency of the results obtained by different authors.

Correlations of Heat Capacity with Molar Volume. The set of 19 ILs was used for exploring of the correlations (Table 4). For these ILs, the heat capacity data with the uncertainty of better than ± 1 % as well as the density data are available. The evaluated density for most ILs was taken from ref 39. The density of [C_{14}mim]NTf_2 at $T = 308.15$ K was determined in ref 40. The value of $(\partial\rho/\partial T)_p = -0.88$ kg·m^{-3}·K^{-1} for this liquid was estimated from the $(\partial V/\partial T)_p$ values for [$C_n$mim]NTf_2 ($n = 2, 4, 6, 8$) assuming they linearly change with the number of carbon atoms in the alkyl chain. The temperature dependence of density for [C_3mim]Br in the temperature range (303 to 358) K was determined in this work to be

$$\rho/\text{kg}\cdot\text{m}^{-3} = 1358.9 - 0.686(T/\text{K} - 298.15) \qquad (3)$$

The densities of [C_3mim]Br reported in ref 41 are 3.2 % lower than those calculated from eq 3. The cause of such a large difference is unknown. However, it should be noted that the majority of the expected impurities in [C_3mim]Br will decrease the density of this IL because their density is lower than that of [C_3mim]Br. The data on both heat capacity and density for ILs are available in the temperature range (258 to 370) K, but the most studied temperature range is (290 to 350) K.

It is seen from Table 4 that the molar heat capacities of ILs at $T = 298.15$ K differ by more than two times. The temperature dependence $C_p(T)$ is also different: the dC_p/dT values are from (0.33 to 0.74) J·K^{-2}·mol^{-1}. The thermal coefficient of heat capacity $(1/C_p)(dC_p/dt)$ is more stable and changes by less than 25 %: from (0.95·10^{-3} to 1.48·10^{-3}) K^{-1}.

The dependence of the specific heat capacities of ILs on the molecular structure is less pronounced (Table 4). The average value is $c_p(298.15\text{ K}) = 1.53 \pm 0.09$ J·K^{-1}·g^{-1}, and the deviations from this value are within ± 26 %. When the temperature increases, the specific heat capacity of ILs raises proportionally dC_p/dT. At $T = 350$ K the average specific value is $c_p = 1.62 \pm 0.10$ J·K^{-1}·g^{-1}, and the deviations from this value do not exceed ± 27 %.

The volumic heat capacity of ILs C_p/V is much more stable. Its average value at $T = 298.15$ K is

$$C_p/V = 1.95 \pm 0.02\ \text{J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3} \qquad (4)$$

This value is in a good agreement with ref 2. The deviation of the heat capacities from this value is less than ± 5 % (Table 4), and this deviation can be an estimate of the error inherited in the correlation but not related to the uncertainties in the experimental data. The largest deviation is observed for [C_3mim]Br and [C_4mim]AcO.

Since $(1/C_p)(dC_p/dt)$ and $(1/V)(dV/dT)$ for ILs are positive and comparable quantities, one can assume that the temperature dependence of C_p/V for these liquids will be less pronounced than that of c_p^2. This is confirmed in this work: at $T = 350$ K, $C_p/V = 2.00 \pm 0.02$ J·K^{-1}·cm^{-3}. The largest deviation of 4.2 % is observed for [C_2mim]$EtSO_4$ (Table 4). If one uses the whole data set the following equation can be obtained:

$$(C_p/V)/\text{J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3} = 1.951 + 8.33\cdot 10^{-4}((T/\text{K}) - 298.15) \qquad (5)$$

The standard error of regression is 0.03 J·K^{-1}·cm^{-3}, and the largest deviation is −4.9 %.

The used data set contains imidazolium, ammonium, and pyrrolidinium ILs with various anions such as BF_4^-, PF_6^-, $EtSO_4^-$, TfO^-, NTf_2^-, and so forth. So, the obtained results are expected to be general for ILs but not molecular liquids. The

Table 4. Heat Capacity of ILs

no.	compound	C_p[a] $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	ρ $\mathrm{kg \cdot m^{-3}}$	c_p $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	C_p/V $\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$	C_p $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	ρ $\mathrm{kg \cdot m^{-3}}$	c_p $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	C_p/V $\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$
		$T = 298.15$ K				$T = 350$ K			
1	$[C_2mim]BF_4$	308.1[b]	1.279	1.556	1.990	327.3	1.252	1.653	2.069
2	$[C_2mim]EtSO_4$	382.8[c]	1.237	1.620	2.003	407.5	1.206	1.725	2.079
3	$[C_2mim]NTf_2$	506.9[d]	1.518	1.295	1.966	532.0	1.466	1.360	1.993
4	$[C_3mim]Br$	280.8[c]	1.359	1.369	1.860	299.2	1.323	1.459	1.930
5	$[C_4mim]BF_4$	367.0[c]	1.202	1.624	1.953	391.5	1.166	1.732	2.020
6	$[C_4mim]AcO$	383.2[e]	1.053	1.933	2.035	409.0		2.063	
7	$[C_4mim]CF_3COO$	407.9[e]	1.217	1.617	1.968	433.0		1.717	
8	$[C_4mim]N(CN)_2$	375.7[c]	1.059	1.831	1.939	396.1	1.031	1.930	1.989
9	$[C_4mim]NTf_2$	565.7[f]	1.438	1.349	1.939	595.0	1.389	1.419	1.970
10	$[C_4mim]PF_6$	408.5[g]	1.365	1.437	1.962		1.323		
11	$[C_4mim]OTf$	427.7[c]	1.298	1.484	1.926	455.4	1.259	1.580	1.989
12	$[C_6mim]BF_4$	431.0[h]	1.145	1.696	1.943		1.110		
13	$[C_6mim]NTf_2$	631.6[i]	1.372	1.412	1.936	662.8	1.325	1.481	1.963
14	$[C_8mim]BF_4$	497.8[c]	1.105	1.765	1.950	530.3	1.072	1.880	2.015
15	$[C_8mim]NTf_2$	693.0[j]	1.321	1.458	1.925	731.4	1.273	1.538	1.958
16	$[C_{14}mim]NTf_2$	c				936.5	1.170	1.673	1.957
17	$[BuMe_3N]NTf_2$	559.3[c]	1.392	1.411	1.964	590.3	1.346	1.489	2.005
18	$[C_3MePrl]NTf_2$	554.0[b]	1.433	1.357	1.944	588.4	1.384	1.441	1.994
19	$[C_4MePrl]NTf_2$	588.0[c]	1.401	1.392	1.950	624.2	1.355	1.478	2.002
	average values:			1.53 ± 0.09	1.95 ± 0.02			1.62 ± 0.10	2.00 ± 0.02

[a] Sources of C_p data are stated in this column. [b] Ref 22. [c] This work. [d] Refs 3 and 6. [e] Ref 38. [f] Refs 5 to 7 and 36. [g] Refs 9 and 36. [h] Ref 37. [i] Refs 4 and 8. [j] Ref 3.

volumic heat capacity of molecular liquids strongly depends on their molecular structure and exceeds 4 $\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$ for water.

The constancy of C_p/V can be used for evaluation of the uncertainties of the heat capacity measurements. For example, according to ref 42, the heat capacity of $[C_1mim]MeSO_4$ is $C_p = 366 \pm 1\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at $T = 350$ K. The density of this IL at the noted temperature is $1291 \pm 2\ \mathrm{kg \cdot m^{-3}}$.[39] The volumic heat capacity $C_p/V = 2.27\ \mathrm{J \cdot K^{-1} \cdot cm^{-3}}$ is 13 % above the average value for ILs. Since such a large error is hardly possible in the density measurements, the heat capacity of $[C_1mim]MeSO_4$ should be remeasured.

We analyzed the linear correlations of the molar heat capacity with the molar volume of ILs. The following equation was obtained for $T = 298.15$ K:

$$C_p/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 8.6 + 1.915(V/\mathrm{cm^3 \cdot mol^{-1}}) \tag{6}$$

The standard error of the regression was 6.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and the maximum deviation was −6.0 %. For the whole set, it was found that the equation

$$C_p/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 7.7 + 0.226((T/\mathrm{K}) - 298.15) + 1.918(V/\mathrm{cm^3 \cdot mol^{-1}}) \tag{7}$$

describes the experimental data with the standard error of 6.2 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and the maximum deviation of −6.0 %. Thus, correlations 6 and 7 do not have advantage over simpler eqs 4 and 5 for volumic heat capacity.

ILs possess a high enough volumic heat capacity for their effective application in heat accumulators.[43] C_p/V was demonstrated in this work to be almost independent of the composition of IL. Therefore, the heat-accumulating IL should be chosen subject to the other parameters: thermal stability, heat conductivity, viscosity, and so forth.

Conclusion

In this work the heat capacities of nine ILs were measured by adiabatic calorimetry. With the use of these and literature data on heat capacity and density for nineteen ILs it was found that at a given temperature the volumic heat capacity of ILs remains constant within ± 5 %. It was demonstrated that the volumic heat capacity of ILs linearly changes with temperature in the range of (258 to 370) K. It was found that the selection of IL for technical applications is limited not by the heat capacity but by the other parameters. The correlations proposed in this work can be used for technical applications and for checking of the mutual consistency of the data on the heat capacity of ILs.

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Supporting Information Available:

The tables of the experimental heat capacities, the temperature ranges of the available C_p and ρ data for the used IL data set, the experimental density points, and the figure of volumic heat capacity for ILs. This material is available free of charge via the Internet at http://pubs.acs.org.

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